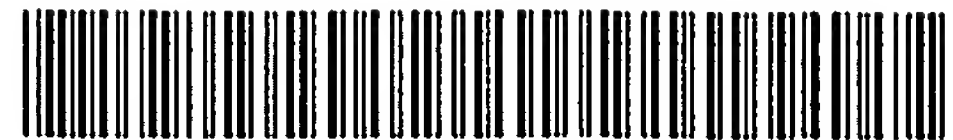


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(54) **Cellulose fiber-containing structure**

Cellulosefasern enthaltendes Flächengebilde

Structure textile contenant des fibres cellulosiques

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DescriptionBackground of the Invention

5 1. Field of the Invention

[0001] The present invention relates to a cellulose fibers-containing structure having shape stability and antimicrobial property excellent in industrial washing durability.

10 2. Description of Related Arts

[0002] Antimicrobial fiber structures are widely used in various clothes, interlinings, linings, bedclothes, interior products, etc. Especially in recent years, the intra-hospital infection by Methicillin Resistant Staphylococcus Aureus (MRSA) poses a problem, and as a countermeasure, white overalls, covers, sheets, curtains, etc. are desired to be antibacterial against MRSA.

[0003] However, since materials used in this area are frequently industrially washed usually at 60 to 85°C, few conventional techniques can provide those having sufficient durability. Furthermore, if those materials contain cellulose fibers, they have a problem that the shape stability becomes poor after washing.

[0004] As conventional antimicrobial treatment, it has mainly been practiced to knead an inorganic antimicrobial agent containing silver, copper or zinc, etc. into synthetic fibers in the stage of spinning as described in Japanese Patent Laid-Open (Kokai) No. Hei9-273073, or to spray or pad an organic antimicrobial agent containing a quaternary ammonium salt, etc. as described in Japanese Patent Laid-Open (Kokai) No. Hei4-11076. The former technique is excellent in view of washing durability, but does not allow fabrics such as woven fabrics and knitted fabrics to be treated. Furthermore, since the antimicrobial agent is precipitated as crystals on the die face in the stage of spinning, there is a problem that yarn breaking occurs often. On the other hand, the latter technique has an advantage that fabrics can be treated to be antimicrobial, but is inferior in view of washing durability of antimicrobial property.

[0005] Furthermore, in the applications as described above, fabrics with high cellulose fiber contents are preferably used since they have high water absorbability and are agreeable to the touch, but on the other hand, they have such disadvantages that they are likely to be creased and shrunk by washing compared to synthetic fiber structures and that it is difficult to let them have antimicrobial property durable against industrial washing. These disadvantages are desired to be overcome.

Summary of the Invention

[0006] The object of this invention is to provide a cellulose fibers-containing structure having antimicrobial property excellent in industrial washing durability, and also having shape stability such as crease resistance and shrinkage resistance.

[0007] The constitution of this invention is as follows.

[0008] A fiber structure comprising cellulose fibers crosslinked by using a crosslinking agent and synthetic fibers, characterized in that the crosslinking index represented by the following formula of the cellulose fibers is in a range of 1 to 4, and that the synthetic fibers contain an antimicrobial agent having an inorganic value/organic value ratio of 0.3 to 1.4.

$$\text{Crosslinking index} = A - B$$

45 where A is the coefficient of moisture absorption of the fiber structure after crosslinking in an atmosphere of 30°C and 90% RH (%), and B is the coefficient of moisture absorption of the fiber structure after crosslinking in an atmosphere of 20°C and 65% RH (%).

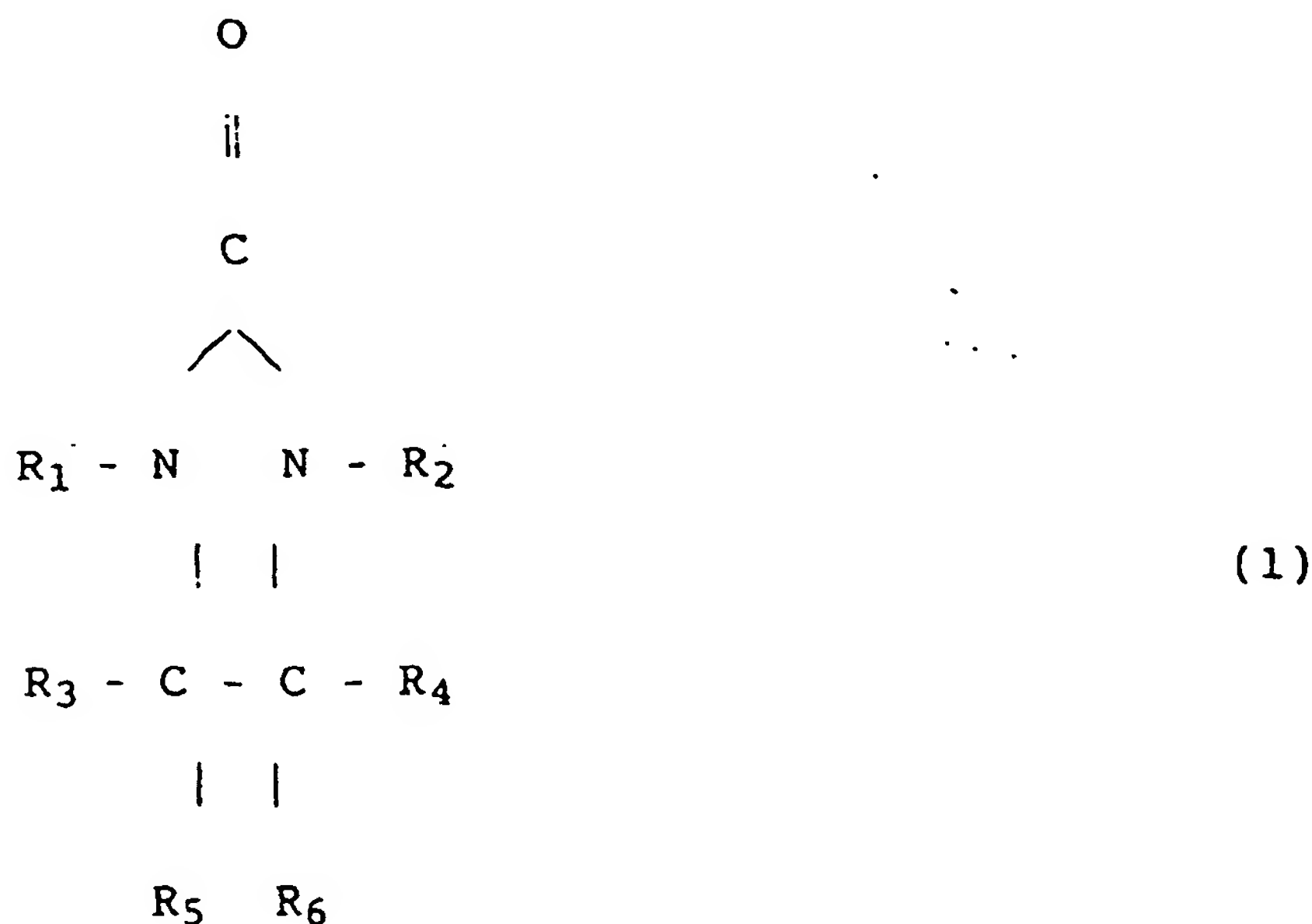
[0009] Furthermore, it is preferable that the cellulose fibers are crosslinked and modified by using a specific nitrogen-containing polyfunctional compound, and that the synthetic fibers have a pyridine based antimicrobial agent fixed and exhausted into the fibers.

Description of the Preferred Embodiments

55 [0010] The cellulose fiber-containing structure referred to in this invention can be not only a fabric but also a band, string, thread, etc. respectively formed by fibers. It can have any structure and shape, but a fabric, i.e., a woven fabric, knitted fabric or nonwoven fabric respectively containing cellulose fibers is preferable.

[0011] The cellulose fibers in this invention include natural cellulose fibers such as cotton, hemp and pulp, regenerated cellulose fibers such as viscose rayon, etc.

[0012] In this invention, the cellulose fibers are crosslinked and modified by a crosslinking agent. The crosslinking agent refers to a compound which reacts with the hydroxyl groups in the cellulose molecules constituting the cellulose fibers, particularly the hydroxyl groups in an amorphous region causing creasing and shrinkage at the time of washing, for forming a crosslinked structure across and in the cellulose molecules. The crosslinking agents which can be used include formaldehyde, dimethylolethyleneurea, dimethyloltriazine, dimethyloluron, dimethylolglyoxalmonouren, dimethylpropyleneurea, cellulose reactive resins obtained by methoxylating or ethoxylating some or all of the methylol groups of these compounds, polycarboxylic acids, isocyanates, etc. Among these crosslinking agents, for efficiently and effectively crosslinking and modifying cellulose fibers, formaldehyde or a nitrogen-containing polyfunctional compound represented by the following general formula (I) can be preferably used.



where R_1 and R_2 denote, respectively independently, -H, alkyl group with 1 to 4 carbon atoms or CH_2OR_7 ; $\text{R}_3, \text{R}_4, \text{R}_5$ and R_6 denote, respectively independently, -H or $-\text{OR}_8$; and R_7 and R_8 denote, respectively independently, -H or alkyl group with 1 to 4 carbon atoms.

[0013] As for the modification degree of cellulose fibers, the crosslinking index defined by the following formula must be in a range of 1 to 4. A preferable range is 2 to 3.5. The crosslinking index is calculated by subtracting the value of the coefficient of moisture absorption of the crosslinked and modified cellulose fibers in an atmosphere of 20°C and 65% RH from the value of the coefficient of absorption in an atmosphere of 30°C and 90% RH, and it is an index for knowing how far the cellulose fibers are crosslinked and modified. That is, the index is based upon the fact that the hydroxyl groups in the cellulose molecules are blocked by crosslinking modification to lower the coefficient of moisture absorption. The smaller the index, the larger the degree of crosslinking modification, and the larger the index, the smaller the degree of crosslinking modification. Generally, the crosslinking index of unprocessed cotton and hemp is about 4 to 5.

$$\text{Crosslinking index} = A - B$$

where A is the coefficient of moisture absorption of the fiber structure after crosslinking in an atmosphere of 30°C and 90% RH (%), and B is the coefficient of moisture absorption of the fiber structure after crosslinking in an atmosphere of 20°C and 65% RH (%).

[0014] If the crosslinking index is smaller than 1, the crosslinked structure is formed excessively to lower the strength and flexibility of the fabric, and though the fabric is good in shape stability, it cannot be practically used. On the other hand, if the crosslinking index is larger than 4, the crosslinking modification of cellulose fibers is insufficient, and the required level of shape stability such as crease resistance and shrinkage resistance cannot be imparted. Considering the balance among the strength, flexibility and shape stability of the fabric, it is preferable that the crosslinking index is in a range of 2 to 3.5.

[0015] The nitrogen-containing polyfunctional compound refers to a compound having nitrogen and two or more functional groups. The compounds which can be used here include, for example, dimethylolethyleneurea, methylated dimethyloluron, dimethylolpropyleneurea, dimethyloldihydroxyethyleneurea, 4-methoxy-5-dimethylpropyleneurea dimethylolation product, methylated trimethylolmelamine, dimethylolalkyltriazones, dimethylolurea, hexamethylolmelamine, tetramethylolacetylenediurea, etc.

[0016] For adding any of these crosslinking agents to cellulose fibers, any of various means can be applied. Particularly, the crosslinking agent can be applied as a gas, or by padding, immersion, spraying, printing, coating, gravure processing or foam processing, etc. When the crosslinking agent is a cellulose reactive resin, polycarboxylic acid or isocyanate, etc., padding can be preferably used.

[0017] In the crosslinking modification of cellulose fibers, for the purpose of promoting the reaction of the crosslinking agent, a catalyst can also be preferably used together, and for example, an organic acid, organic amine salt, or a metal salt such as magnesium chloride, zinc nitrate, zinc borofluoride, magnesium nitrate or zinc chloride, etc. can be used.

[0018] For crosslinking modification of cellulose fibers by a crosslinking agent, any ordinary crosslinking modification method can be applied. A pre-cure method in which a crosslinking agent is added to a fiber structure formed as a fabric, followed by heat treatment can be used, though this invention is not limited to the method. It is preferable that the heat treatment temperature is 80 to 220°C. A more preferable range is 120 to 200°C.

[0019] The cellulose fibers heat-treated like this have the nitrogen-containing polyfunctional compound combined with cellulose molecules, to have antimicrobial property very high in industrial washing durability, and show a microbicidal activity value (Standard Test Method: JIS L 1902) of larger than 0.

[0020] The synthetic fibers which can be used in this invention include polyester fibers of polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, etc., acrylic fibers, polyamide fibers of nylon 6, nylon 66, etc. The fiber structure of this invention can be yarns, woven fabric or nonwoven fabric, etc. Among these synthetic fibers, polyester fibers can provide a fiber structure most excellent in the industrial washing durability of antimicrobial property.

[0021] The fiber structure of this invention must have the cellulose fibers and the synthetic fibers mixed as mixed fibers, mix-spun fibers, mixed woven fabric or mixed knitted fabric, etc. In addition, wool, silk, etc. can also be mixed. For securing effective shape stability, it is preferable that the cellulose fibers are contained in an amount of 10 to 90 wt% based on the total weight of fibers.

[0022] In this invention, the synthetic fibers contain an antimicrobial agent with an inorganic value/organic value ratio of 0.3 to 1.4. A preferable antimicrobial agent is a pyridine based antimicrobial agent having a molecular weight of 200 to 700 and an average particle size of 2 μm or less.

[0023] A pyridine based antimicrobial agent strongly adheres to or is exhausted and diffused into the synthetic fibers. It is considered that if the antimicrobial agent is made closer to a disperse dye to be exhausted and diffused into fibers, in three factors of molecular weight, inorganic value/organic value ratio and average particle size, it shows behavior similar to that of the disperse dye. If these factors are not satisfied, the antimicrobial agent does not strongly adhere or is not exhausted or diffused into the synthetic fibers, and sufficient industrial washing durability cannot be obtained.

[0024] If the molecular weight is less than 200, the washing durability tends to be low though the antimicrobial agent adheres to or is exhausted and diffused into the synthetic fibers. On the other hand, if the molecular weight is more than 700, the antimicrobial agent is unlikely to adhere to or to be exhausted into the synthetic fibers.

[0025] A preferable molecular weight range of the antimicrobial agent is 300 to 500.

[0026] The "inorganic value/organic value ratio" in this invention is an indicator contrived by Minoru Fujita, to express the polarity of various organic compounds in view of organic concept [see Revised Edition, Science of Chemical Experiments, Organic Chemistry, Kawade Shobo (1971)]. For the ratio, the organic value of one carbon (C) atom is taken as 20, and the inorganic and organic values of various polar groups are determined with reference to it, as shown in Table 1. The inorganic value/organic value ratio refers to the ratio of the sum of inorganic values to the sum of organic values.

Table 1

Inorganic groups	Value	Inorganic groups	Value
Light metal salt	>500	>CO	65
Heavy metal salt, amine, ammonium salt	>400	-COOR, -P=P-	60
-AsO ₃ H, -AsO ₂ H	300	>C=NH	50
-SO ₂ NHCO-, -N=N-NH ₂	260	-N=N-	30
-SO ₃ H, -CONIICONIICO-	250	>O	20
-SO ₂ NH-, -CONHCONH-	240	Benzene nucleus (general aromatic single nucleus)	15

Table continued

Inorganic groups	Value	Inorganic groups		Value
-CONHCO-, -CSNH-	230	Non-aromatic ring		10
=NOH	220	Triple bond		3
=N-NH-	210	Double bond		2
-CONII-	200	Organic and inorganic group	Organic value	Inorganic value
-CSSH	180	>SO ₂	40	110
-CSOII, -COSII	160	-SCN	70	80
Anthracene nucleus, phenanthrene nucleus	155	-NCS	70	75
-COOH	150	-NO ₂	70	70
Lactone	120	-CN	40	70
-CO-O-CO-	110	-NO	50	50
-OII, -As-O-As-	100	-ONO ₂	60	40
-Hg(organic)	95	-NC	40	40
-COSR, -OSOR, -AS=AS-	90	-NCO	30	30
Naphthalene nucleus	85	-I	60	20
-NH-NII-, -O-CO-O-	80	-Br, -SH, -S-	40	20
-NH ₂ , -NHR, -NR ₂	70	-C.I, -P	20	20
Note: In the above inorganic groups, each carbon atoms is counted as an organic values of 20. For SO ₂ group and those enumerated below it, the value is already included in the organic value.				

[0027] According to this organic concept, for example, the inorganic value/organic value ratio of polyethylene terephthalate can be calculated as 0.7. In this invention, attention is paid to the affinity between synthetic fibers and an antimicrobial agent based on the value calculated according to the organic concept, and an antimicrobial agent with the inorganic value/organic value ratio kept in a predetermined range is caused to adhere to or to be exhausted and diffused into the synthetic fibers.

[0028] If the inorganic value/organic value ratio is less than 0.3, the organic property is too strong, and on the contrary if more than 1.4, the inorganic property is too strong. In both the cases, the antimicrobial agent is unlikely to adhere to or to be exhausted and diffused into the synthetic fibers. It is preferable that the inorganicvalue/organicvalueratio is 0.35 to 1. 3. Amore preferable range is 0.4 to 1.2.

[0029] For example, in the case of 2,3,5,6-tetrachloro-4-hydroxypyridine, since it has one benzene nucleus, four -Cl groups, one -OH group and one -NR₂ group, the inorganic value is 265. On the other hand, since it has five C (carbon) atoms and four -Cl groups, the organic value is 180. Hence the inorganic value/organic value ratio is 1.47. In the case of 2-pyridylthiol-1-oxide zinc, it exists as a chelate complex, and in view of electronegativity, zinc and sulfur are considered to be covalent-bonded. So, according to the calculation, the compound has an inorganic value of 85 and an organic value of 190, and an inorganic value/organic value ratio of 0.45. On the other hand, in the case of a further pyridine based antimicrobial agent, 2-pyridylthiol-1-oxide sodium, the difference between sodium and sulfur in electronegativity is more than 1.6, and their bond is an ionic bond. In this case, since sodium acts as a light metal salt, it can be calculated that the inorganic value is 585, that the organic value is 190, and that the inorganic value/organic value ratio is 3.0. So, the compound is poor in affinity to polyesters.

[0030] In this invention, among such antimicrobial agents, any one having an average particle size of 2 μm or less is used. If the average particle size is more than 2 μm, it is unlikely to adhere to or to be exhausted into the synthetic fibers, and in addition, if it is formed into a treating liquid, the particles settle to show a tendency of poor liquid stability. It is preferable that the average particle size of the antimicrobial agent is 1 μm or less.

[0031] The antimicrobial agents which can be used here include pyridine compounds such as 2-chloro-6-trichloromethylpyridine, 2-chloro-4-trichloromethyl-6-methoxypyridine, 2-chloro-4-trichloromethyl-6-(2-furylmethoxy)pyridine, di(4-chlorophenyl)pyridylmethanol, 2,3,5-trichloro-4-(n-propylsulfonyl)pyridine, 2-pyridylthiol-1-oxide zinc and di(2-pyridylthiol-1-oxide), etc. Among them, especially 2-pyridylthiol-1-oxide zinc is preferable since it is good in affinity to fibers, can

adhere to or be exhausted into fibers, hence good in washing durability and effective against a wide range of microbes including MRSA.

[0032] Moreover, it is preferable that the fiber structure of this invention has an microbicidal activity value of larger than 0 when measured according to the microbiostatic evaluation method (Standard Test Method: JIS L 1902) established by SEK (Japan Association for the Functional Evaluation of Textiles) still after 50 times of industrial washing treatment at 80°C for 12 minutes using a wash liquor containing a surfactant. It is most preferable that the microbicidal activity value is larger than 0 when measured according to the microbiostatic evaluation method (Standard Test Method: JIS L 1902) established by SEK (New Function Evaluation Council for Textile Products) still after 50 times of industrial washing treatment at 85°C for 15 minutes using a wash liquor containing a peroxide, strong alkali and surfactant.

[0033] The wash liquor containing a peroxide, strong alkali and surfactant is prepared, for example, by supplying 2 g/l of detergent "Zabu" (registered trademark) produced by Kao Corp. as the surfactant, 3 cc/l of hydrogen peroxide water (35% for industrial use) as the peroxide and 1.5 g/l of sodium percarbonate as the strong alkali, into a drum dyeing machine filled with water at a bath ratio of 1: 20. The wash liquor is then heated to 85°C, and the antimicrobial fiber structure of this invention and waste cloth are supplied into it, to be washed for 15 minutes. The waste water is discharged, and the fiber structure is dehydrated and washed with overflowing water for 10 minutes, and dehydrated. This is one time of washing. The washing is repeated 50 times, and the fiber structure is dried using a tumbler dryer for 20 minutes, for microbiostatic evaluation.

[0034] For letting the antimicrobial agent adhere to or be exhausted into the synthetic fibers, the fiber structure is immersed in a solution containing the antimicrobial agent in a jet dyeing machine, etc., and heated at atmospheric pressure or under pressurization at 90 to 160°C for 10 to 120 minutes, preferably at 120 to 135°C for 20 to 60 minutes. In this case, if necessary, a disperse dye or disperse fluorescent whitening agent can also be added to the solution.

[0035] In this method, it is preferable to effect dry heat treatment by a tenter, etc. at 160 to 200°C for 15 seconds to 5 minutes, more preferably at 170 to 190°C for 30 seconds to 2 minutes, after completion of the treatment in the solution. This dry heat treatment allows the antimicrobial agent to be diffused into the fibers annularly from the surfaces of the fibers, to allow the washing durability to be improved without impairing the antimicrobial property. These treatment conditions can be changed to control such states as the adhesion of the antimicrobial agent to the surfaces of fibers, the annular distribution in the fibers and the diffusion in the fibers.

[0036] As another method, after the solution containing the antimicrobial agent is caused to adhere to the fiber structure by padding or spraying, etc., the fiber structure can be heat-treated by dry heat treatment or wet heat treatment at 160 to 200°C for 30 seconds to 10 minutes, preferably 170 to 190°C for 1 to 5 minutes using a tenter, etc.

[0037] In view of cost and rationalization of processing, it is preferable that after letting the crosslinking agent and the antimicrobial agent adhere to the fiber structure by padding or spraying, etc., the fiber structure is heat-treated at 170 to 190°C for 30 seconds to 5 minutes, though the present invention is not limited to this method.

[0038] In this invention, for the purpose of improving the softness of the fabric, it is preferable to add a silicone based softening agent. However, if a generally used silicone based softening agent is used, or especially if an amino modified silicone based softening agent mainly composed of an aminoalkyl group-containing polysiloxane is used for treating the fabric, the treated fabric has water repellency though it can have excellent softness and softness durability, and so the treatment is unsuitable for obtaining a cellulose fibers-containing fabric having shape stability such as crease resistance and shrinkage resistance, and also water absorbability as intended in this invention.

[0039] Therefore, in this invention, a silicone based softening agent which gives a soft look and taste to the fabric without impairing the water absorbability of the fabric is preferable. Particularly a softening agent mainly consisting of an organopolysiloxane containing both amino groups and polyoxyalkyl groups in one molecule and a polyethylene polyamine higher fatty acid type amide compound containing an amine or at least one group capable of reacting with a hydroxyl group in one molecule is preferable.

[0040] The organopolysiloxane is not especially limited as far as it is an organopolysiloxane containing both amino groups and polyoxyalkyl groups in one molecule, i.e., an amino polyether modified silicone. However, an organopolysiloxane having a viscosity of 100 to 100,000 cst at 25°C and an amino equivalent of 300 to 3000 is preferable. Some or all of the amino groups of the amino polyether modified silicone can be blocked by a compound reactive with the amino groups, an organic acid or the anhydride or chloride, etc. of an organic acid for prevention of yellowing.

[0041] The polyethylene polyamine higher fatty acid type amide compound can be, for example, any of reaction products between any of polyethylene polyamine higher fatty acid amides, urea condensation products of polyethylene polyamine higher fatty acid amides and imidazolium salts of polyethylene polyamine higher fatty acid type amide portions, and any of dicarboxylic acids, cyclic acid anhydrides, diglycidyl ethers, diisocyanates, etc.

[0042] The polyethylene polyamines which can be used as a component of these compounds include diethylenetriamine, triethylenetetramine, tetraethylenepentamine, aminoethylethanolamine, etc. The higher fatty acids which can be used here are generally those derived from natural oils and fats such as palm oil, beef tallow, rapeseed oil, rice bran oil and fish oil, but chemically synthesized higher fatty acids can also be used. Among them, higher fatty acids having an iodine value of 50 or less and 12 to 24 carbon atoms are preferable. The dicarboxylic acids and cyclic acid anhydrides

include maleic acid, maleic anhydride, fumaric acid, malic acid, succinic acid, succinic anhydride, tartaric acid, phthalic acid, phthalic anhydride, etc. The diglycidyl ethers include ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, polyoxyalkylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, etc. The diisocyanates include aromatic diisocyanates such as tolylene diisocyanate, xylene diisocyanate and diphenylmethane diisocyanate, aliphatic diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate and lysine diisocyanate, etc.

[0043] The molar ratio of the polyethylene polyamine and the higher fatty acid constituting the polyethylene polyamine higher fatty acid type amide compound is usually 1: 1.0 ~ 2.5, preferably 1: 1.2 - 1.8.

[0044] The ratio by weight of the aminopolyether modified silicone and the polyethylene polyamine higher fatty acid amide as the main ingredients of the silicone based softening agent is 1 : 0.2 - 1.5, preferably 1: 0.3 - 1.0. If the polyethylene polyamine higher fatty acid amide is less than 0.2, sufficient softness cannot be obtained, and if more than 1.5, the treated fabric declines in water absorbability, which is not preferred.

[0045] It is preferable that the deposited amount of the silicone based softening agent is 0.06 to 1.0 wt% based on the weight of the fibers. If the deposited amount is less than 0.06 wt%, it is difficult to impart sufficient softness and smoothness to the fabric, and if more than 1.0 wt%, such defects as texture dislocation are caused though the softness and smoothness are improved.

[0046] In this invention, for the purpose of improving the water absorbability of the fabric, it is preferable to add a hydrophilic resin, particularly a hydrophilic polyester resin. As such a resin, a resin mainly composed of a polyalkylene glycol-polyester block copolymer can be preferably used.

[0047] The polyalkylene glycol referred to here has a main chain of $-C_nH_{2n}O-$ ($n = 2 - 4$) in the molecule, and particularly can be polyethylene glycol, polypropylene glycol or a block copolymer thereof, etc. It is preferable that the molecular weight of the polyalkylene glycol is 300 to 40000. A more preferable range is 1000 to 10000. If the molecular weight is less than 300, the durability of deposition in the fibers tends to be insufficient, and if more than 40000, the dispersibility tends to decline.

[0048] The polyester which can be used for producing the block copolymer of a polyalkylene glycol consists of an aromatic dicarboxylic acid and an alkylene glycol. The aromatic dicarboxylic acids which can be used here include, for example, terephthalic acid, lower alkyl esters of and terephthalic acid, isophthalic acid and lower alkyl esters of isophthalic acid. The alkylene glycols which can be used here include, for example, ethylene glycol, propylene glycol, butylene glycol, etc.

[0049] It is preferable that the deposited amount of the hydrophilic polyester resin is 0.03 to 1.0 wt% based on the weight of the fibers. If the deposited amount is less than 0.03 wt%, the effect of adding the hydrophilic polyester resin is small, and if more than 1.0 wt%, the fabric gives a slimy feeling while the color fastness declines though the water absorbability of the fabric is improved.

[0050] In this invention, a vinylsulfonic acid polymer can be preferably fixed to the fiber structure, to make it hygroscopic.

[0051] The vinylsulfonic acid polymers which can be used in this invention include homopolymers and copolymers of vinylsulfonic acid monomers such as 2-acrylamido-2-methylpropanesulfonic acid, styrenesulfonic acid, isoprenesulfonic acid, allylsulfonic acid and methallylsulfonic acid, and also copolymers consisting of any of these vinylsulfonic acid monomers and a crosslinking agent. As the crosslinking agent of the vinylsulfonic acid polymer, a polyfunctional vinyl monomer which makes the produced polymer three-dimensional can be preferably used. Furthermore, if a vinylsulfonic acid polymer is crosslinked by a crosslinking agent, high washing durability can be obtained.

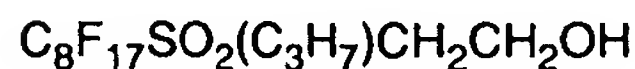
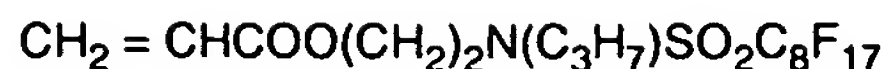
[0052] Moreover, the sulfonate group ends of the vinylsulfonic acid polymer can be substituted by at least one kind of metal ions selected from Na^+ , Ni^+ , Cu^{2+} , Zn^{2+} , Mn^{2+} , Ag^+ and Fe^{2+} , for preventing that the cellulose fibers are made brittle or discolored by an acid. Furthermore, in this invention, it is preferable that the amount of the vinylsulfonic acid polymer to be fixed is 1 to 20% owf in view of hygroscopicity, durability and look & taste, and also in view of excellent hygroscopicity and moisture retention.

[0053] In this invention, it is also preferable that the fiber structure is made water-repellent by depositing a polyfluoroalkyl group-containing acrylic copolymer, silicone resin, which may be an aminosilicone resin, and aminoplast resin and/or polyfunctional block isocyanato group-containing urethane resin in the fiber structure.

[0054] The polyfluoroalkyl group-containing acrylic copolymers which can be used here are not especially limited, and include, for example, homopolymers of vinyl monomers having a polyfluoroalkenyl group with 3 to 20 carbon atoms or a polyfluoroalkyl group, and copolymers consisting of any of such vinyl monomers and another vinyl monomer having neither polyfluoroalkenyl group nor polyfluoroalkyl group.

[0055] The vinyl monomers having a polyfluoroalkenyl group or polyfluoroalkyl group which can be used here include, for example,





10 [0056] The other vinyl monomers having neither polyfluoroalkenyl group nor polyfluoroalkyl group include, for example, ethylene, vinyl chloride, vinylidene chloride, acrylamide, styrene, benzyl acrylate, vinyl alkyl ketone, maleic anhydride, isoprene, siloxane and block isocyanates. Among them, an acrylic copolymer mainly composed of a copolymer containing a block isocyanate as a vinyl monomer is suitable. It is preferable that the polyfluoroalkyl group-containing acrylic copolymer is present in an amount of 0.01 to 10% owf based on the amount of the fiber fabric. An especially preferable
15 range is 0.03 to 5% owf.

[0057] The aminoplast resins which can be used in this invention include, for example, melamine resins such as trimethylolmelamine resin and hexamethylolmelamine resin, urea resins such as dimethylolpropyleneurea resin, dimethylolethyleneurea resin and dimethylolhydroxyurea resin, uron resins such as dimethyloluron resin. Among them, hexamethylolmelamine resin is suitable. It is preferable that the amount of the aminoplast resin is 0.01 to 2 wt% as the solid
20 content based on the weight of the fiber fabric. An especially preferable range is 0.02 to 1 wt%.

[0058] When an aminoplast resin is used, a generally used catalyst can also be used. The catalysts which can be used here include ammonium, aluminum and zinc salts of inorganic acids such as phosphoric acid, sulfuric acid and nitric acid, and salts of organic acids such as formic acid, acetic acid, acrylic acid and succinic acid.

[0059] As the polyfunctional block isocyanato group-containing urethane resin in this invention, any organic compound containing two or more block isocyanato functional groups in the molecule can be used without any limitation, and it can be a polyfunctional block isocyanate urethane resin obtained by reaction with a phenol, diethyl malonate, methyl ethyl ketone oxime or sodium bisulfite, etc. to allow reproduction of active isocyanato groups by dissociation when heated.

[0060] Especially preferable is a water dispersion of methyl ethyl ketoxime of diphenylmethane diisocyanate or of methyl ethyl ketoxime of trimethylolpropane tolylene diisocyanate adduct.

30 [0061] It is preferable that the amount of the polyfunctional block isocyanate urethane resin is 0.01 to 4 wt% as the solid content based on the weight of the fiber fabric. An especially preferable range is 0.03 to 1 wt%.

[0062] Furthermore, a catalyst can also be used to promote the lowering of the dissociation temperature of the polyfunctional block isocyanato group-containing urethane resin, and dibutyltin dioleate, dibutyltin stearate, stearyl zinc or an organic amine compound can be preferably used as the catalyst.

35 [0063] In this invention, a photocatalyst semiconductor composed of a compound oxide of titanium and silicon can be preferably fixed to the fiber structure using at least one binder selected from alkyl silicate resins, silicone resins and fluorine resins, to impart deodorizability and odor impregnation preventability to the fiber structure.

[0064] In this invention, the photocatalyst semiconductor has a nature of oxidizing and decomposing organic substances by the strong oxidizing power excited by ultraviolet light, and particularly can be a semiconductor having a crystal
40 structure called anatase, rutile or brookite.

[0065] In this invention, attention is paid to the fact that such a photocatalyst semiconductor has deodorizability, coloring matter decomposing and removing capability (antifouling property) and antimicrobial property (antibacterial and antifungal property). Formaldehyde is generated after the cellulose fibers are crosslinked and modified by a crosslinking agent such as formaldehyde or cellulose reactive resin, to impart shape stability such as crease resistance and shrinkage
45 resistance to the cellulose fibers, and also formaldehyde is liberated at the time of crosslinking, to remain in the fabric. The photocatalyst semiconductor is used to oxidize and decompose such formaldehyde, so that the fabric obtained may be excellent in crease resistance and very small in the concentration of formalin produced to remain as a result of decomposition of the crosslinking agent, preferably as small as 20 ppm or less, and furthermore may have deodorizability, antifouling property and microbicidal capability.

50 [0066] The photocatalyst semiconductor of this invention removes the tobacco smell and the body smell due to sweat, etc. in good balance, which are difficult to remove by conventional techniques. Furthermore, since it can oxidize and decompose such odors, it can prevent the fabric from being impregnated with any odor as an unprecedentedly very excellent effect. Moreover, since it can decompose and remove coloring matters such as the tar of tobacco, it can manifest an antifouling effect against coloring matters. In addition, since the photocatalyst semiconductor of this invention
55 has microbicidal power against MRSA, Escherichia coli, Staphylococcus aureus, etc., it can also manifest an effect in antimicrobial and antifungal finishing.

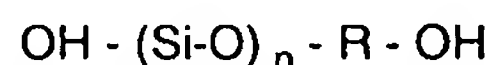
[0067] If the photocatalyst semiconductor is too large in particle size or too small in specific surface area, the rate of decomposing organic substances, particularly bacteria tends to decline. As for the deodorizing reaction, offensive odor

components are adsorbed by the photocatalyst semiconductor, and later decomposed by the oxidizing power generated by the excitation of the photocatalyst semiconductor caused by ultraviolet light. In this case, whether offensive odor components can be adsorbed well or not greatly affects the deodorizing efficiency. So, a photocatalyst semiconductor with a primary particle size of 20 nm or less and a specific surface area of 100 to 300 m²/g can be preferably used. If the amount of the photocatalyst semiconductor deposited in the fiber structure is too small, the rate at which organic substances such as offensive odor components are decomposed declines not allowing a sufficient effect to be obtained. If too large on the contrary, the fiber fabric is deteriorated by the oxidation of the photocatalyst semiconductor and becomes hard in taste and look unpractically, and furthermore, the fibers themselves and binder, etc. are decomposed by the oxidative decomposition of the photocatalyst semiconductor, to issue an offensive odor disadvantageously. So, it is preferable that the deposited amount of the photocatalyst semiconductor is 0.05 to 30 wt% based on the weight of the fiber structure. A more preferable range is 0.05 to 20 wt%, and an especially preferable range is 0.08 to 10 wt%.

[0068] As the photocatalyst semiconductor of this invention, it is preferable to use a compound oxide of titanium and silicon. As the compound oxide, the compound oxide produced according to the method described in Japanese Patent Publication (Kokoku) No. Hei5-55184 can be used. In general, a binary compound oxide of titanium and silicon is known as a solid acid as described, for example, in "Catalysts" (Vol 17. No. 3, Page 72, 1975), and shows remarkable acidity which cannot be observed in the respective oxides constituting the compound oxide, having a high surface area. That is, the compound oxide of titanium and silicon is not a simple mixture consisting of titanium oxide and silicon oxide, and when a binary oxide of titanium and silicon is formed, it manifests peculiar properties. Furthermore, the compound oxide has an amorphous or almost amorphous fine structure if analyzed by X-ray diffraction, and as for the ratio of titanium and silicon, it is preferable that the compound oxide consists of 20 to 95 mol% of titanium oxide and 5 to 80 mol% of silicon oxide. If the rate of silicone oxide is larger than this range, the photocatalyst activity of titanium oxide tends to be weak. So, it is preferable to decide the optimum ratio for each purpose of use.

[0069] In this invention, to deposit any of various photocatalyst semiconductors such as the compound oxide of titanium and silicon in the cellulose fiber-containing fabric, any of various binders such as urethane resins, acrylic resins and cellulose resins can be used. However, preferably, if at least one binder selected from alkyl silicate resins, silicone resins and fluorine resins is used, the decomposition, coloration and offensive odor generation peculiar to organic resins by the oxidation of the photocatalyst semiconductor can be prevented. In such a combination, it is not necessary to form an intermediate layer of an inorganic substance such as titanium peroxide between the fibers and the binder containing the photocatalyst semiconductor, and the photocatalyst semiconductor can be used to dramatically improve the washing durability, taste & look, and also cost.

[0070] An alkyl silicate resin mainly consists of Si-O bond portions and a straight chain or branched chain saturated alkyl group, and has OH groups at both the ends characteristically. That is, it contains a structure represented by the following formula.



[0071] In the above formula, R denotes a straight chain or branched chain saturated alkyl group with 1 to 10 carbon atoms, and n is an integer of 1 or more, preferably in a range of 1000 to 10000 for enhancing the inorganic property.

[0072] The alkyl group is a straight chain or branched chain saturated alkyl group such as methyl group, ethyl group, propyl group or isopropyl group. The alkyl silicate resin used can also be one alkyl silicate resin or a mixture consisting of two alkyl silicate resins. The alkyl silicate resin has a feature that it easily causes dehydration reaction in the presence of heat, to form a polysiloxane film. The alkyl silicate resin is soluble in water, and if the fiber structure is impregnated with an aqueous solution of the alkyl silicate resin, mangled by a mangle, and treated at 200°C or lower, a thin film is formed on the surface of each fiber. It is also possible to make the alkyl silicate resin and the compound oxide of titanium and silicon directly deposited on the surface of fiber structure.

[0073] A binder mixture consisting of a silicone resin and a fluorine resin can also be deposited on the fiber structure. These binders are, as described above, excellent in heat resistance, light resistance and chemicals resistance, and also excellent in durability against the oxidizing power of the photocatalyst semiconductor.

[0074] As the silicone resin, any of condensation crosslinking type resins belonging to silicone resins and silicone varnishes can be used. Products obtained by condensing one or more condensation crosslinking type resins such as tetraethoxysilane and methyltrimethoxysilane can also be used. These resins have a three-dimensional structure and are most excellent in heat resistance and chemicals resistance among silicone resins. If a silicone oxide sol obtained by hydrolyzing tetraisopropoxysilane or tetraethoxysilane by a strong acid in an alcohol/water mixed solvent, a vitreous film can be formed characteristically. The film obtained by such a sol/gel method is close to an inorganic substance and can be preferably used.

[0075] Furthermore, as the fluorine resin, a vinyl ether and/or vinyl ester and a polymerizable fluoroolefin compound can be preferably used since they have very excellent properties. For example, polyvinyl fluoride, polyethylene tetrafluoride, tetrafluoroethylene-perfluoroalkyl vinyl ester, vinyl ester-fluoroolefin, etc. can be preferably used since they are

less decomposed and deteriorated.

[0076] The differences of these silicone resins and fluorine resins from usually often used organic resins such as acrylic resins, urethane resins and epoxy resins are that the former resins contain few hydrocarbon groups likely to be decomposed by heat or chemicals' action, and contain a few hydrocarbon groups such as methyl groups or phenyl groups as the end groups or side chains since the silicone resins are mainly composed of Si-O bonds while the fluorine resins are mainly composed of F-C bonds.

[0077] To the binder, a coupling agent can be further added, to improve the bonding strength between inorganic substances and organic substances, thus allowing chemical bond strength to work among the fibers, binder and photocatalyst semiconductor. As a result, the washing durability can be enhanced.

[0078] As the binder, zeolite can also be added, to improve the capability to adsorb odor components, and to increase the inorganic component ratio in the structure. As a result, there is an effect of inhibiting the decomposition by the photocatalyst. If zeolite containing a precious metal such as gold, platinum, silver or palladium preferably in an amount of 0.01 to 5 wt% is used, the antimicrobial effect can be further enhanced.

[0079] In this invention, if the fiber structure is pre-treated by high pressure water vapor and crosslinked and modified using a crosslinking agent, a crease preventing effect higher than the conventional level can be obtained, and the decline of strength after completion of crosslinking modification which has been a conventional problem can be prevented.

[0080] The high pressure water vapor referred to here is saturated water vapor of high temperature. Particularly, high pressure saturated water vapor with a temperature of 120 to 200° C and a pressure of 2 to 16 kg/cm is preferable. If the temperature is lower than 120 °C, the effect by this treatment is insufficient, and if higher than 200°C, such phenomena as yellowing and embrittlement caused by heat are caused, which is not preferred. The treatment time can be appropriately set in relation with the treatment temperature. Usually it is preferable that the treatment time is 30 seconds to 30 minutes. For the treatment, any pressure vessel capable of withstanding these conditions can be used, and an ordinary autoclave can be used.

[0081] The fiber structure is excellent in the antimicrobial property with industrial washing durability, and also in shape stability, and can be preferably used in the form of a woven fabric or knitted fabric, being suitable for such applications as dress shirts, uniforms, inner socks, interior products and sports clothing.

Examples

[0082] The present invention is described below more particularly in reference to examples.

[0083] In the following examples and comparative examples, the quality was evaluated according to the following methods.

(1) Washing method

[0084] A drum dyeing machine was used to wash using a wash liquor containing 2 g/l of detergent "Zabu" (registered trademark) produced by Kao Corp., 3 cc/l of hydrogen peroxide water (35% for industrial use) and 1.5 g/l of sodium percarbonate at a bath ratio of 1:20 at $85 \pm 2^\circ\text{C}$ for 15 minutes, and the waste water was discharged. The sample fabric was dehydrated and washed with overflowing water for 10 minutes, then being dried using a tumbler dryer for 20 minutes. This was one time of washing.

(2) Antimicrobial test method

[0085] The Standard Test Method (JIS L 1902) was adopted, and a clinically isolated MRSA strain was used. A bouillon suspension of said test strain was injected into a sterilized sample fabric and cultured in an enclosed container at 37°C for 18 hours. The plate counts before and after culture were measured to obtain a plate count increment/decrement as follows.

[0086] The $\log(A/C)$ at $\log(B/A) > 1.5$ was identified as a plate count increment/decrement, hence as an microbicidal activity value. An microbicidal activity value of larger than 0 was judged to be acceptable.

[0087] In the above, A denotes the plate count obtained by inoculating a fabric not containing any antimicrobial agent with the strain and immediately recovering the dispersed strain; B denotes the plate count obtained by inoculating a fabric not containing any antimicrobial agent with the strain, culturing it for 18 hours, and recovering the dispersed strain; and C denotes the plate count obtained by inoculating a fabric containing an antimicrobial agent with the strain, culturing for 18 hours and recovering the dispersed strain.

(3) Evaluation of crease resistance

[0088] Judged based on the 5-stage replica method of AATCC 124-1984. Class 5 (good) - Class 1 (poor)

(4) Washing shrinkage percentage

[0089] Measured according to JIS L 1042.

5 (5) Evaluation of hygroscopicity (ΔMR)

[0090]

$$\Delta MR (\%) = MR2 - MR1$$

where MR1 refers to the hygroscopicity (%) measured after allowing an absolutely dry sample to stand in 20°C 65% RH atmosphere for 24 hours, which corresponds to an environment in a wardrobe, i.e., an environment before wearing, and MR2 refers to the hygroscopicity (%) measured after allowing an absolutely dry sample to stand in 30°C 90% RH atmosphere for 24 hours, which almost corresponds to an environment in the clothing involved in any bodily exercise.

[0091] ΔMR is obtained by subtracting the value of MR1 from the value of MR2, and suggests how much perspiration in the clothing is absorbed when a person wearing the clothing takes bodily exercise. It can be said that a higher ΔMR value suggests amore comfortable condition. In general, it is said that the ΔMR of polyesters is 0%, that of nylons 2%, that of cotton 4%, and that of wool 6%.

20 (6) Water repellency

[0092] Evaluated according to JIS L 1092 (spray method).

- 100: No deposited wetting on the surface.
- 90: Slight deposited wetting on the surface
- 80: Wetting at water dropping points on the surface
- 70: Partial wetting on the entire surface
- 50: Wetting on the entire surface
- 0: Full wetting on the surface

(7) Odor impregnation preventability

[0093] Twenty five microliters of 0.01% isovaleric acid aqueous solution was taken by a micro-syringe and 5 μ l of it was dropped at 5 points in the central region of a 10 cm x 10 cm piece of a fabric; at one point at the center of the fabric and at four points surrounding said one central point, as if to form five spots on a side of a dice. This fabric was allowed to stand under a fluorescent lamp for 3 hours, and smelled by 10 persons for sensory evaluation. The odor in this case was evaluated according to the following criterion, and the mean value was adopted.

- 5: Severe odor
- 4: Strong odor
- 3: Easily sensible odor
- 2: Discernible but feeble odor
- 1: Slightly sensible odor
- 0: No odor

Example 1

[0094] A woven fabric (with an areal unit weight of 185 g/m²) was prepared as a sample fabric by mixing polyethylene terephthalate spun fibers and cotton fibers at 50 : 50 into yarns of 45 yarn number count and using the yarns as warp threads and weft threads.

[0095] This woven fabric was immersed in a treating solution of the following composition (1), padded at a squeeze rate of 80%, preliminarily dried at 130°C for 90 seconds and heat-treated at 180°C for 1 minute, to prepare a sample. At this moment, the antimicrobial agent had been exhausted and diffused into the fibers. The evaluation results are shown in Table 2.

(1) Composition

Crosslinking agent

[0096] Dimethyloldihydroxyethyleneurea resin aqueous solution (solid content 20%)

Catalyst

[0097] Magnesium chloride

Antimicrobial agent

[0098] 2-pyridylthiol-1-oxide zinc (inorganic value/organic value ratio: 0.45, molecular weight: 317, average particle size: 0.5 μm)

[0099] Aminosilicone resin with an amino equivalent of 3000 g/mole (solid content 20%)

Hydrophilic polyester resin

[0100] Polyethylene glycol (molecular weight 3000) copolymer emulsion (solid content 10%) consisting of 500 parts of dimethyl terephthalate and 400 parts of ethylene glycol

[0101] Even after industrial washing, the fabric showed good shape stability and antimicrobial property.

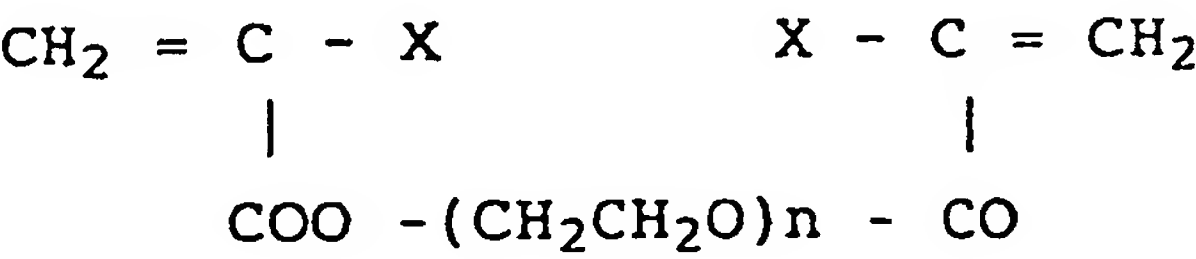
Example 2

[0102] A woven fabric obtained by using 75-denier polyethylene terephthalate yarns respectively consisting of 72 filaments and cotton yarns of 45 yarn number count together at 50 : 50 was used as a sample fabric. The woven fabric was treated as described for Example 1 by a treating solution of the following composition (1), immersed in a treating solution of the following composition (2), mangled by a mangle at a squeezing rate of 40%, dried in a dryer at 120°C for 2 minutes, treated by a 100°C heating steamer for 3 minutes and washed with hot water, to obtain a sample. At this moment, the antimicrobial agent had been exhausted and diffused into the fibers. The evaluation results are shown in Table 2.

(2) Composition

[0103]

Sodium 2-acrylamido-2-methylpropanesulfonate	160 g/l
N-methylolacrylamide	10 g/l
Ammonium persulfate	3 g/l
Monomer represented by the following chemical formula where X denotes a methyl group, and n denotes 23.	30 g/l



(X = H or CH₃, n = an integer of 9 to 23)

[0104] Even after industrial washing, the fabric showed good shape stability and antimicrobial property, and even after 10 times of household washing, the fabric showed good hygroscopicity.

Example 3

[0105] The woven fabric as used in Example 1 was used as a sample fabric and immersed in a treating solution of the following composition (3), padded at a squeezing rate of 80%, preliminarily dried at 130° C for 90 seconds and heat-treated at 180°C for 1 minute, to prepare a sample. At this moment, the antimicrobial agent had been exhausted and

diffused into the fibers. The evaluation results are shown in Table 2.

(3) Composition

5 Crosslinking agent

[0106] Dimethyloldihydroxyethyleneurea resin aqueous solution (solid content 20%)

Catalyst

10

[0107] Magnesium chloride

Antimicrobial agent

15

[0108] 2-chloro-4-trichloromethyl-6-(2-furylmethoxy)pyridine (inorganic value/organic value ratio: 0.73, molecular weight: 329, average particle size: 0.7 μm)

Silicone resin

20

[0109] Aminosilicone resin with an amino equivalent of 3000 g/mole (solid content 20%)

Hydrophilic polyester resin

25

[0110] Polyethylene glycol (molecular weight 3000) copolymer emulsion (solid content 10%) consisting of 500 parts of dimethyl terephthalate and 400 parts of ethylene glycol

Fluorine based water repellent

30

[0111] Copolymer (solid content 30%) obtained by copolymerization reaction of the following compounds and distilled water

35	$\text{C}_{12}\text{F}_{25}(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$	88 g
	$\text{CH}_3(\text{C}_2\text{H}_5)\text{CNONCH}(\text{C}_6\text{H}_4)\text{CH}_2(\text{C}_6\text{H}_4)\text{NHCOO}(\text{CH}_2)\text{CH}=\text{CH}_2$	1 g
	Stearyl acrylate	9 g
	Vinyl chloride	4 g
	Stearylmethylammonium chloride	2 g
	$\text{C}_{12}\text{H}_{25}\text{O}(\text{C}_2\text{H}_4\text{O})_{12}\text{H}$	2.4 g
	Acetone	60 g
40	Distilled water	415 g
	Amine based catalyst	0.8 g

Aminoplast resin

45

[0112] Hexamethylolmelamine resin (solid content 80%)

Catalyst

50

[0113] Organic amine compound Polyfunctional block isocyanato group-containing urethane resin

[0114] Water dispersion (solid content 30%) of methyl ethyl ketoxime of diphenylmethane diisocyanate

Catalyst

55

Dibutyltin dioleate

[0115] Even after industrial washing, the fabric showed good shape stability and antimicrobial property, and even after 10 times of washing, it, showed good water repellency.

Example 4

[0116] A broad woven fabric with an areal unit weight of 112 g/m² consisting of 45% of polyester yarns of 45 yarn number count and 55% of cotton yarns respectively scoured and marcerized according to conventional methods was used. The woven fabric was treated as described for Example 1, immersed in a treating solution of the following composition (4) obtained by using an aqueous dispersion of a compound oxide of titanium and silicon (concentration 20%) with an average particle size of 0.3 μm obtained from a compound oxide of titanium and silicon with an average primary particle size of 7 nm and an average specific surface area of 150 m²/g, as a photocatalyst, padded at a squeezing rate of 80%, preliminarily dried at 130°C for 90 seconds and heat-treated at 180° C for 1 minute, to prepare a sample. At this moment, the antimicrobial agent had been exhausted and dispersed into the fibers. The evaluation results are shown in Table 2.

(4) Composition

[0117]

Alkyl silicate resin (concentration 20%)	1.0 wt%
Silicone resin (concentration 45%)	1.5 wt%
Silane coupling agent (concentration 100%)	0.2 wt%
Zeolite carrying a precious metal (concentration 20%)	0.3 wt%
Compound oxide of titanium and silicon (concentration 20%)	1.0 wt%

[0118] Even after industrial washing, the fabric had good shape stability and antimicrobial property, and also had good deodorizability and odor permeation preventability.

Example 5

[0119] Three rolls (each about 25 yards) of the woven fabric used in Example 4 were wound around a 110 cm wide 100 mm dia. bobbin, and treated by high pressure water vapor in an autoclave at 180°C at 2 a pressure of 9.4kg/cm for 3 minutes. The woven fabric was immersed in a treating solution containing 70 g/l of dimethyloldihydroxyethyleneurea resin aqueous solution (solid content 20%) as a crosslinking agent and 10 g/l of magnesium chloride as a catalyst, padded at a squeezing rate of 80%, preliminarily dried at 100°C for 2 minutes and heat-treated at 170° C for 1 minute. At this moment, the antimicrobial agent had been exhausted and diffused into the fibers. The evaluation results are shown in Table 2.

[0120] Even after industrial washing, the fabric had good shape stability and antimicrobial property.

Comparative Example 1

[0121] A sample fabric as used in Example 1 was treated by a treating solution of the following composition (5), to prepare a sample. The evaluation results are shown in Table 2.

(5) Composition

Antimicrobial agent

[0122] 2-pyridylthiol-1-oxide zinc

Silicone resin

[0123] Aminosilicone resin with an amino equivalent of 3000 g/mole (solid content 20%)

Hydrophilic polyester resin

[0124] Polyethyleneglycol(molecular weight3000)copolymer emulsion (solid content 10%) consisting of 500 parts of dimethyl terephthalate and 400 parts of ethylene glycol

Comparative Example 2

[0125] A sample fabric as used in Example 2 was treated by a treating solution of the following composition (6), to prepare a sample. At this moment, the antimicrobial agent had not been exhausted into the fibers. The evaluation results are shown in Table 2.

(6) Composition

Crosslinking agent

[0126] Dimethyloldihydroxyethyleneurea resin aqueous solution (solid content 20%)

Catalyst

[0127] Magnesium chloride

Antimicrobial agent

[0128] Methyl 6-(2-thiophenecarbonyl)-1H-2-benzimidazolecarbamate (inorganic value/organic value ratio: 1.52, molecular weight: 302, average particle size: 0.5 μm)

Silicone resin

[0129] Aminosilicone resin with an amino equivalent of 3000 g/mole (solid content 20%)

Hydrophilic polyester resin

[0130] Polyethylene glycol (molecular weight 3000) copolymer emulsion (solid content 10%) consisting of 500 parts of dimethyl terephthalate and 400 parts of ethylene glycol

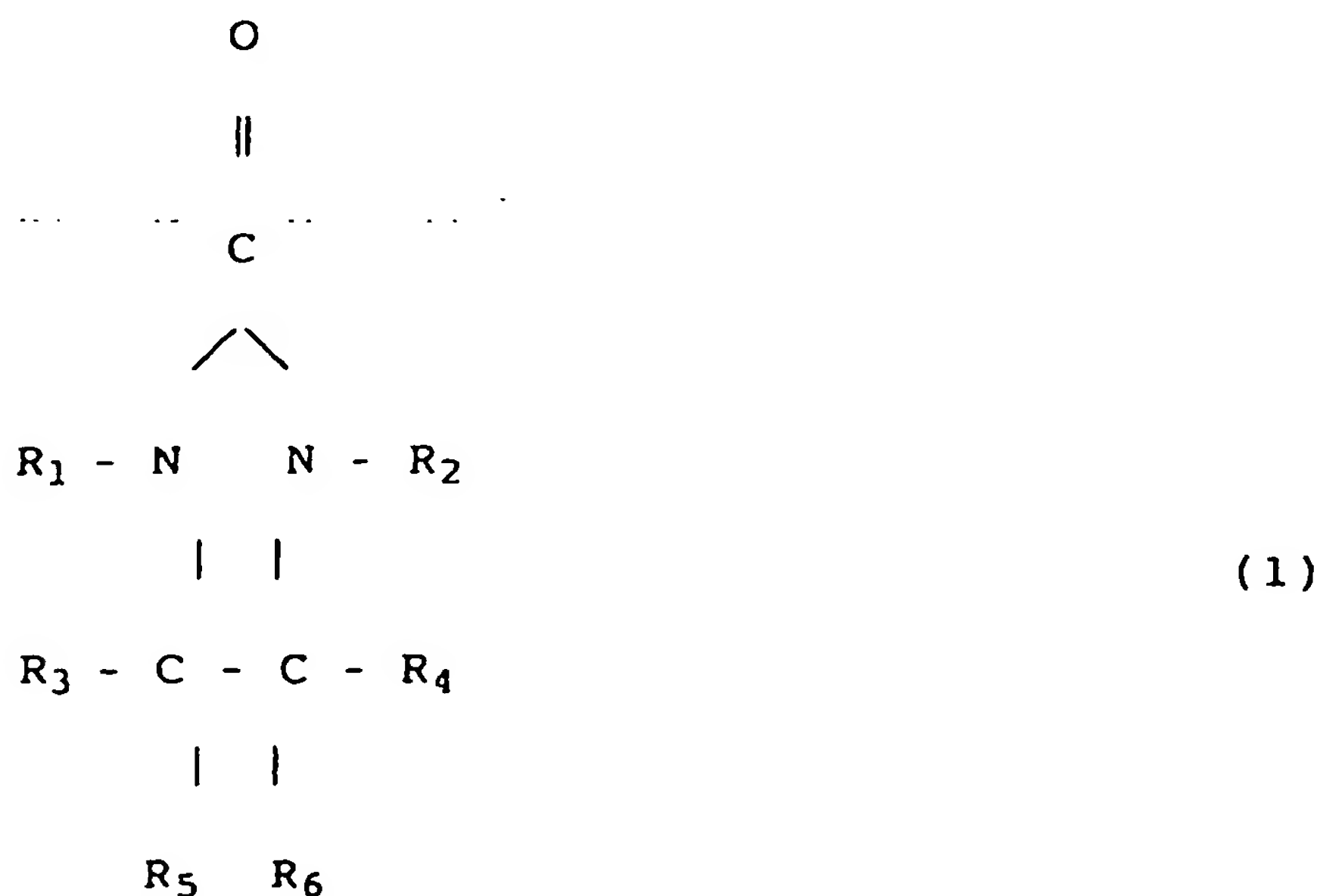
[0131] In Comparative Example 1, since the crosslinking index did not satisfy the condition of claim 1 because of no crosslinking agent used, the shape stability was poor. In Comparative Example 2, since the inorganic value/organic value ratio of the antimicrobial agent did not satisfy the condition of claim 1, the antimicrobial property after washing was poor.

Table 2

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1	Comparative Example 2
Crosslinking index	3.4	3.3	3.2	3.4	3.5	4.5	2.0
Crease resistance (class)	4	4	4	4	4-5	1-2	-
Washing shrinkage percentage (%)	0.2	3.0	0.2	0.2	0.2	4.0	3.4
	0.1	2.8	0.1	0.1	0.1	3.0	3.0
Antimicrobial property (microbicidal activity value)	3.0	2.8	3.3	3.2	3.0	3.0	-0.2
Hygroscopicity (ΔMR)	Before washing	4.0	-	-	-	-	-
	After washing	2.5	-	-	-	-	-
Water repellency	Before washing	-	1.00	-	-	-	-
	After washing	-	70+	-	-	-	-
Deodorizability (marks) (isovaleric acid odor)	Before washing	-	-	0.5	-	-	-
	After washing	-	-	1.0	-	-	-

Claims

1. A cellulose fiber-containing structure comprising cellulose fibers crosslinked by using a crosslinking agent and synthetic fibers, **characterized in that** the crosslinking index of the cellulose fibers is in a range of 1 to 4, and that the synthetic fibers contain an antimicrobial agent having an inorganic value/organic value ratio of 0.3 to 1.4 which crosslinking index is represented by the following formula: Crosslinking index = A - B
where A is the coefficient of moisture absorption of the fiber structure after crosslinking in an atmosphere of 30°C and 90% RH (%), and B is the coefficient of moisture absorption of the fiber structure after crosslinking in an atmosphere of 20°C and 65% RH (%).
2. A cellulose fiber-containing structure according to claim 1, wherein the molecular weight of the antimicrobial agent is 200 to 700.
3. A cellulose fiber-containing structure according to claim 1 or 2, wherein the average particle size of the antimicrobial agent is 2 μm or less.
4. A cellulose fiber-containing structure according to any one of claims 1 to 3, wherein the antimicrobial agent is a pyridine based antimicrobial agent.
5. A cellulose fiber-containing structure according to claim 4, wherein the pyridine based antimicrobial agent is at least one selected from 2-chloro-6-trichloromethylpyridine, 2-chloro-4-trichloromethyl-6-methoxypyridine, 2-chloro-4-trichloromethyl-6-(2-furylmethoxy)pyridine, di(4-chlorophenyl)pyridylmethanol, 2,3,5-trichloro-4-(n-propylsulfonyl)pyridine, 2-pyridylthiol-1-oxide zinc and di(2-pyridylthiol-1-oxide).
6. A cellulose fibers-containing structure according to claim 5, wherein the pyridine based antimicrobial agent is 2-pyridylthiol-1-oxide zinc.
7. A cellulose fiber-containing structure according to any one of claims 1 to 6, wherein the antimicrobial agent adheres to or is exhausted into the synthetic fibers.
8. A cellulose fiber-containing structure according to any one of claims 1 to 7, which contains the cellulose fibers in an amount of 10 to 90 wt% based on the total weight of the fibers.
9. A cellulose fiber-containing structure according to any one of claims 1 to 8, wherein the crosslinking agent is a nitrogen-containing polyfunctional compound represented by the following general formula (1):



where R_1 and R_2 denote, respectively independently, -H, alkyl group with 1 to 4 carbon atoms or $-\text{CH}_2\text{OR}_7$; R_3 , R_4 , R_5 and R_6 denote, respectively independently, -H or OR_8 ; and R_7 and R_8 denote, respectively independently, -H or alkyl group with 1 to 4 carbon atoms.

- 5 10. A cellulose fiber-containing structure according to any one of claims 1 to 9, wherein the crosslinking agent is combined with cellulose and the microbicidal activity value (Standard Test Method: JIS L 1902) of the structure after industrial washing is larger than 0.
- 10 11. A cellulose fiber-containing structure according to any one of claims 1 to 10, wherein the synthetic fibers are made of a polyester.
- 15 12. A cellulose fiber-containing structure according to any one of claims 1 to 11, which further contains each of a silicone based softening agent mainly composed of an organopolysiloxane containing both amino groups and polyoxyalkyl groups in one molecule and a polyethylene polyamine higher fatty acid type amide compound containing an amine or at least one group capable of reacting with a hydroxyl group.
- 20 13. A cellulose fiber-containing structure according to claim 12, wherein the polyethylene polyamine higher fatty acid type amide compound is obtained by letting a polyethylene polyamine and a higher fatty acid and at least one compound selected from lower dicarboxylic acids, cyclic acid anhydrides, lower diglycidyl ethers and diisocyanates react with each other.
- 25 14. A cellulose fiber-containing structure according to claim 12 or 13, which contains said silicone based softening agent in an amount of 0.06 to 1.0 wt% based on the weight of the fibers.
- 30 15. A cellulose fiber-containing structure according to any one of claims 1 to 14, which further contains a hydrophilic polyester resin mainly composed of a polyalkylene glycol-polyester block copolymer.
- 35 16. A cellulose fiber-containing structure according to claim 15, wherein the polyalkylene glycol-polyester block copolymer is contained in an amount of 0.03 to 1.0 wt% based on the weight of the fibers.
- 40 17. A cellulose fiber-containing structure according to any one of claims 1 to 16, wherein a vinylsulfonic acid polymer is fixed on the surface of the fiber structure in an amount of 1 to 20%.
- 45 18. A cellulose fiber-containing structure according to claim 17, wherein the vinylsulfonic acid polymer is obtained from at least one monomer selected from 2-acrylamido-2-methylpropanesulfonic acid, styrenesulfonic acid, isoprenesulfonic acid, allylsulfonic acid and methallylsulfonic acid.
- 50 19. A cellulose fiber-containing structure according to any one of claims 1 to 16, wherein a polyfluoroalkyl group-containing acrylic copolymer, silicone resin which may be an aminosilicone resin, and aminoplast resin and/or polyfunctional block isocyanate group-containing urethane resin are deposited on the surface of the fiber structure.
- 55 20. A cellulose fiber-containing structure according to anyone of claims 1 to 16, which has a photocatalyst semiconductor and a binder on the surface.
21. A cellulose fiber-containing structure according to claim 20, wherein the photocatalyst semiconductor is a compound oxide of titanium and silicon.
22. A cellulose fiber-containing structure according to claim 20 or 21, wherein the binder is at least one binder selected from alkyl silicate resins, silicone resins and fluorine resins.
23. A cellulose fiber-containing structure according to any one of claims 1 to 22, wherein the cellulose fibers are pre-treated by high pressure water vapor.
24. A cellulose fiber-containing structure, according to claim 23, wherein the high pressure water vapor is high pressure saturated water vapor of 120 to 200°C.

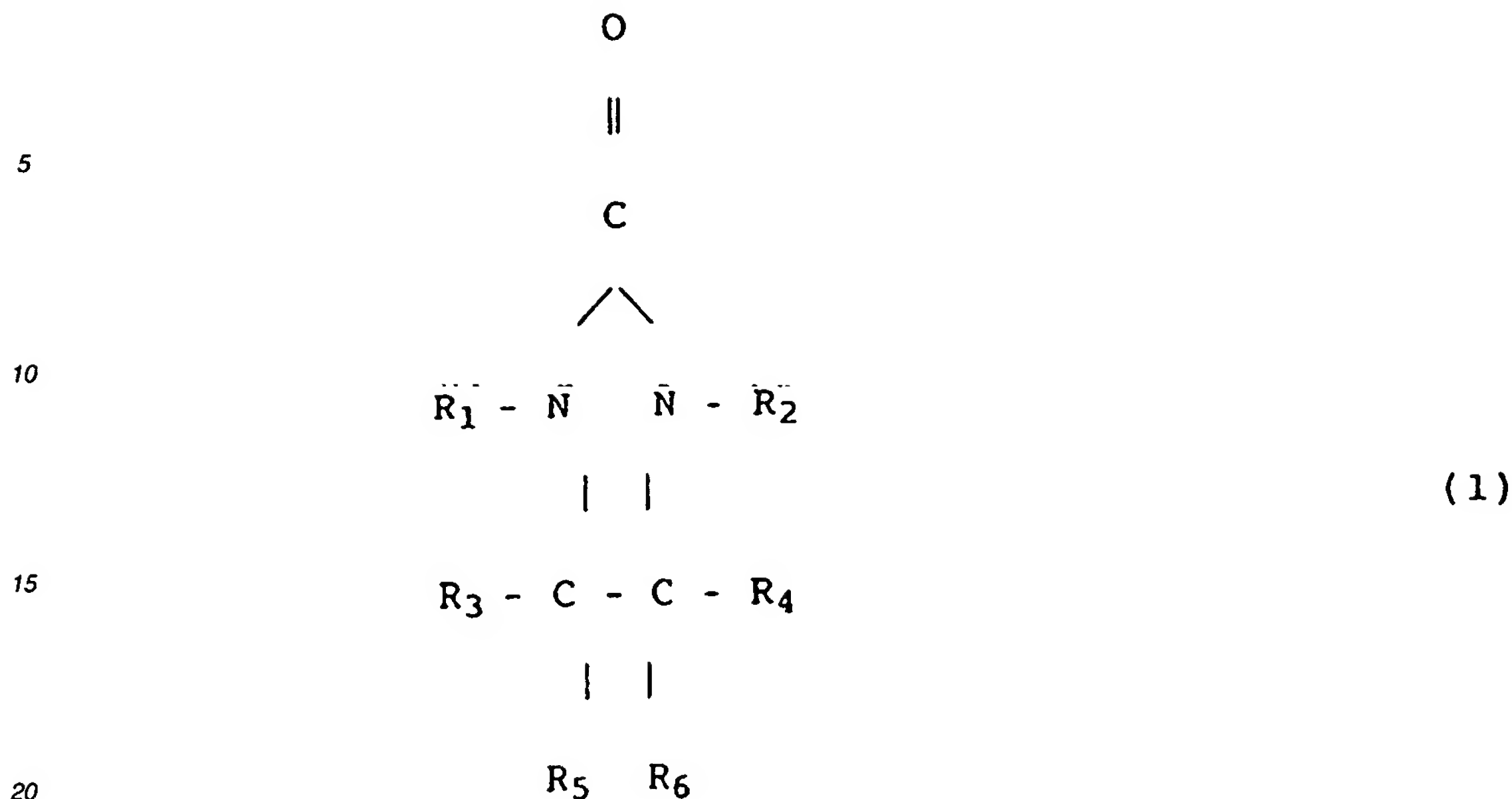
Revendications

1. Structure contenant des fibres de cellulose comprenant des fibres de cellulose réticulées en utilisant un agent réticulant et des fibres synthétiques, **caractérisée en ce que** l'indice de réticulation des fibres de cellulose est dans une gamme de 1 à 4, et **en ce que** les fibres synthétiques contiennent un agent anti-microbien ayant un rapport valeur inorganique/valeur organique de 0,3 à 1,4, lequel indice de réticulation est représenté par la formule qui suit :

$$\text{indice de réticulation} = A - B$$

où A est le coefficient d'absorption d'humidité de la structure des fibres après réticulation dans une atmosphère de 30°C et 90 % HR (%), et B est le coefficient d'absorption d'humidité de la structure des fibres après réticulation dans une atmosphère de 20°C et 65 % HR (%).

2. Structure contenant des fibres de cellulose selon la revendication 1, où le poids moléculaire de l'agent anti-microbien est de 200 à 700.
3. Structure contenant des fibres de cellulose selon la revendication 1 ou 2, où la dimension moyenne des particules de l'agent anti-microbien est de 2 µm au moins.
4. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 3, où l'agent anti-microbien est un agent anti-microbien à base de pyridine.
5. Structure contenant des fibres de cellulose selon la revendication 4, où l'agent anti-microbien à base de pyridine en est au moins un sélectionné parmi 2-chloro-6-trichlorométhylpyridine, 2-chloro-4-trichlorométhyl-6-méthoxypyridine, 2-chloro-4-trichlorométhyl-6-(2-furylméthoxy) pyridine, di(4-chlorophényl) pyridylméthanol, 2,3,5-trichloro-4-(n-propylsulfonyl)pyridine, 2-pyridylthiol-1-oxyde zinc et di (2-pyridylthiol-1-oxyde).
6. Structure contenant des fibres de cellulose selon la revendication 5, où l'agent anti-microbien à base de pyridine est 2-pyridylthiol-1-oxyde zinc.
7. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 6, où l'agent anti-microbien adhère à ou est échappé dans les fibres synthétiques.
8. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 7, qui contient les fibres de cellulose en une quantité de 10 à 90 % en poids en se basant sur le poids total des fibres.
9. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 8, où l'agent réticulant est un composé polyfonctionnel contenant de l'azote représenté par la formule générale (1) qui suit :



où R_1 et R_2 désignent, respectivement indépendamment, -H, un groupe alkyle avec 1 à 4 atomes de carbone ou $-\text{CH}_2\text{OR}_7$; R_3 , R_4 , R_5 et R_6 désignent, respectivement indépendamment, -H ou OR_8 ; et R_7 et R_8 désignent, respectivement indépendamment, -H ou un groupe alkyle avec 1 à 4 atomes de carbone.

10. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 9, où l'agent réticulant est combiné à la cellulose et la valeur d'activité microbienne (Méthode de Test Standard : JIS L 1902) de la structure après lavage industrielle est plus grande que 0.
11. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 10, où les fibres synthétiques sont faites d'un polyester.
12. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 11, qui contient de plus chacun d'un agent assouplissant à base de silicone principalement composé d'un organopolysiloxane contenant à la fois des groupes aminés et des groupes polyoxyalkyles dans une molécule et un composé d'amide du type acide gras supérieur de polyéthylène polyamine contenant une amine ou au moins un groupe capable de réagir avec un groupe hydroxyle.
13. Structure contenant des fibres de cellulose selon la revendication 12, où le composé d'amide du type acide de gras supérieur de polyéthylène polyamine est obtenu en laissant une polyéthylène polyamine et un acide gras supérieur et au moins un composé sélectionné parmi acides dicarboxyliques inférieurs, anhydrides d'acides cycliques, diglycidyl éthers inférieurs et diisocyanates réagir l'un avec l'autre.
14. Structure contenant des fibres de cellulose selon la revendication 12 ou 13, qui contient ledit agent assouplissant à base de silicone en une quantité de 0,06 à 1,0 % en poids en se basant sur le poids des fibres.
15. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 14, qui contient de plus une résine de polyester hydrophile principalement composée d'un copolymère séquencé de polyalkylène glycol-polyester.
16. Structure contenant des fibres de cellulose selon la revendication 15, où le copolymère séquencé de polyalkylène glycol-polyester est contenu en une quantité de 0,03 à 1,0 % en poids en se basant sur le poids des fibres.
17. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 16, où un polymère d'acide vinyle sulfonique est fixé à la surface de la structure des fibres en une quantité de 1 à 20 %.
18. Structure contenant des fibres de cellulose selon la revendication 17, où le polymère d'acide vinyle sulfonique est obtenu à partir d'au moins un monomère sélectionné parmi acide 2-acrylamido-2-méthylpropanesulfonique, acide

styrènesulfonique, acide isoprènesulfonique, acide allyl-sulfonique et acide méthallylsulfonique.

19. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 16, où un copolymère acrylique contenant un groupe polyfluoroalkyle, une résine de silicone qui peut être une résine d'aminosilicone et une résine aminoplaste et/ou une résine uréthane contenant un groupe isocyanate bloc polyfonctionnel sont déposés à la surface de la structure des fibres.
20. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 16, qui a un semi-conducteur photocatalyseur et un liant à la surface.
21. Structure contenant des fibres de cellulose selon la revendication 20, où le semi-conducteur photocatalyseur est un oxyde composé de titane et silicium.
22. Structure contenant des fibres de cellulose selon la revendication 20 ou 21, où le liant est au moins un liant sélectionné parmi des résines de silicate d'alkyle, des résines de silicone et des résines de fluor.
23. Structure contenant des fibres de cellulose selon l'une quelconque des revendications 1 à 22, où les fibres de cellulose sont prétraitées par vapeur d'eau à haute pression.
24. Structure contenant des fibres de cellulose selon la revendication 23, où la vapeur d'eau à haute pression est une vapeur d'eau à haute pression saturée à une température de 120 à 200°C.

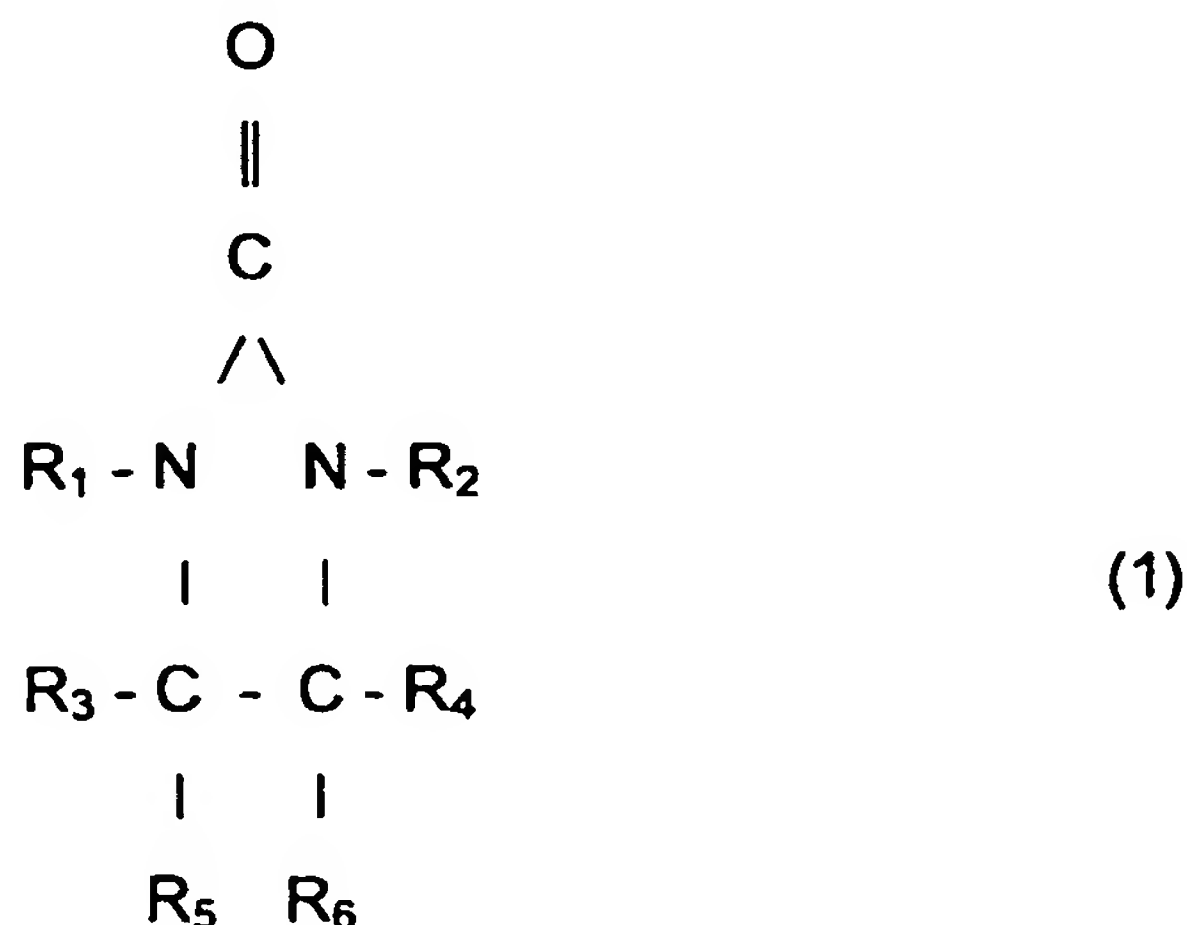
Patentansprüche

1. Cellulosefasern enthaltende Struktur, umfassend Cellulosefasern, die unter Verwendung eines Vernetzers vernetzt wurden, und Synthesefasern, **dadurch gekennzeichnet, dass** der Vernetzungsindex der Cellulosefasern in einem Bereich von 1 bis 4 liegt und dass die Synthesefasern ein antimikrobielles Mittel mit einem Verhältnis zwischen anorganischem Wert und organischem Wert von 0,3 bis 1,4 enthalten, wobei der Vernetzungsindex durch die folgende Formel dargestellt ist:

$$\text{Vernetzungsindex} = A - B$$

- worin A der Feuchtigkeitsabsorptionskoeffizient der Faserstruktur nach dem Vernetzen in einer Atmosphäre mit 30°C und 90 % r.L. ist (%) und B der Feuchtigkeitsabsorptionskoeffizient der Faserstruktur nach dem Vernetzen in einer Atmosphäre mit 20°C und 65 % r.L. ist (%).
2. Cellulosefasern enthaltende Struktur nach Anspruch 1, worin das Molekulargewicht des antimikrobiellen Mittels 200 bis 700 beträgt.
3. Cellulosefasern enthaltende Struktur nach Anspruch 1 oder 2, worin die mittlere Teilchengröße des antimikrobiellen Mittels 2 µm oder weniger beträgt.
4. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 3, worin das antimikrobielle Mittel ein antimikrobielles Mittel auf Pyridinbasis ist.
5. Cellulosefasern enthaltende Struktur nach Anspruch 4, worin das antimikrobielle Mittel auf Pyridinbasis zumindest eines von 2-Chlor-6-trichlormethylpyridin, 2-Chlor-4-trichlormethyl-6-methoxypyridin, 2-Chlor-4-trichlormethyl-6-(2-furylmethoxy)pyridin, Di(4-chlorphenyl)pyridylmethanol, 2,3,5-Trichlor-4-(n-propylsulfonyl)pyridin, 2-Pyridylthiol-1-oxid-zink und Di(2-pyridylthiol-1-oxid) ist.
6. Cellulosefasern enthaltende Struktur nach Anspruch 5, worin das antimikrobielle Mittel auf Pyridinbasis 2-Pyridylthiol-1-oxid-zink ist.
7. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 6, worin das antimikrobielle Mittel auf Pyridinbasis an den Synthesefasern haftet oder in diese eingesaugt ist.

8. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 7, welche die Cellulosefasern, bezogen auf das Gesamtgewicht der Fasern, in einer Menge von 10 bis 90 Gew.-% enthält.
9. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 8, worin der Vernetzer eine stickstoffhaltige polyfunktionelle Verbindung der folgenden allgemeinen Formel (1) ist:



- worin R_1 und R_2 unabhängig voneinander jeweils für -H, eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen oder $-\text{CH}_2\text{OR}_7$ steht;
 R_3 , R_4 , R_5 und R_6 unabhängig voneinander jeweils für -H oder OR_8 stehen; und
 R_7 und R_8 unabhängig voneinander jeweils für -H oder eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen stehen.
10. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 9, worin der Vernetzer mit Cellulose kombiniert ist und der Wert der mikrobiellen Aktivität (Standardtestverfahren JIS L 1902) der Struktur nach industriellem Waschen größer als 0 ist.
11. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 10, worin die Synthesefasern aus Polyester bestehen.
12. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 11, die außerdem einen Weichmacher auf Siliconbasis, der hauptsächlich aus einem Organopolysiloxan mit sowohl Aminogruppen als auch Polyoxyalkylgruppen pro Molekül besteht, und eine Amidverbindung vom höheren Polyethylenpolyaminfettsäuretyp, die ein Amin oder zumindest eine zur Umsetzung mit einer Hydroxylgruppe fähige Gruppe enthält, aufweist.
13. Cellulosefasern enthaltende Struktur nach Anspruch 12, worin die Amidverbindung vom höheren Polyethylenpolyaminfettsäuretyp erhalten wird, indem ein Polyethylenpolyamin und eine höhere Fettsäure mit zumindest einer aus niedrigeren Dicarbonsäuren, zyklischen Säureanhydriden, niedrigeren Diglycidylethern und Diisocyanaten ausgewählten Verbindung umgesetzt werden.
14. Cellulosefasern enthaltende Struktur nach Anspruch 12 oder 13, die den Weichmacher auf Siliconbasis in einer Menge von 0,06 bis 1,0 Gew.-%, bezogen auf das Gewicht der Fasern, umfasst.
15. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 14, die außerdem ein hydrophiles Polyesterharz umfasst, das hauptsächlich aus einem Polyalkylenglykol-Polyester-Blockcopolymer besteht.
16. Cellulosefasern enthaltende Struktur nach Anspruch 15, worin das Polyalkylenglykol-Polyester-Blockcopolymer, bezogen auf das Gewicht der Fasern, in einer Menge von 0,03 bis 1,0 Gew.-% enthalten ist.
17. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 16, worin ein Vinylsulfonsäurepolymer in einer Menge von 1 bis 20 % auf der Oberfläche der Faserstruktur fixiert ist.

18. Cellulosefasern enthaltende Struktur nach Anspruch 17, worin das Vinylsulfonsäurepolymer aus zumindest einem aus 2-Acrylamido-2-methylpropansulfonsäure, Styrolsulfonsäure, Isoprensulfonsäure, Allylsulfonsäure und Methallylsulfonsäure ausgewählten Monomer erhalten wird.

5 19. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 16, worin ein Polyfluoralkylgruppen enthaltendes Acryl-Copolymer, Siliconharz, das ein Aminosiliconharz sein kann, und ein Aminoplastharz und/oder ein polyfunktionelle Isocyanatgruppen enthaltendes Blockurethanharz auf der Oberfläche der Faserstruktur aufgetragen sind.

10 20. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 16, die einen Photokatalysatorhalbleiter und ein Bindemittel auf der Oberfläche aufweist.

21. Cellulosefasern enthaltende Struktur nach Anspruch 20, worin der Photokatalysatorhalbleiter ein Oxidgemisch von Titan und Silicium ist.

15 22. Cellulosefasern enthaltende Struktur nach Anspruch 20 oder 21, worin das Bindemittel zumindest ein aus Alkylsilicatharzen, Siliconharzen und Fluorharzen ausgewähltes Bindemittel ist.

20 23. Cellulosefasern enthaltende Struktur nach einem der Ansprüche 1 bis 22, worin die Cellulosefasern mit Hochdruckwasserdampf vorbehandelt sind.

24. Cellulosefasern enthaltende Struktur nach Anspruch 23, worin der Hochdruckwasserdampf gesättigter Hochdruckwasserdampf mit 120 bis 200 °C ist.

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(54) Title: COMPOSITIONS COMPRISING POLYSILOXANES AND FURTHER POLYMERS

(57) Abstract: Aqueous dispersions comprising polyorganosiloxanes having relatively long alkyl groups and having aromatic groups and also polymers having perfluoroalkyl groups or fluorine-free polyurethanes are useful for treating textile fabrics.



WO 02/100950 A1

Compositions comprising polysiloxanes and further polymers

This invention relates to compositions, especially in the form of aqueous dispersions. These comprise a polyorganosiloxane which contains alkyl groups and aromatic groups in side chains. The aqueous dispersions further comprise a fluoropolymer or a polyurethane. This invention further relates to the use of these dispersions for treating fiber materials.

It is known to treat fiber materials, for example textile fabrics, with aqueous dispersions of polyorganosiloxanes as part of the finishing operation. Textiles can acquire a pleasantly soft hand and/or water-repellent properties as a result.

Polysiloxanes containing alkyl groups and aromatic groups are already known, for example from EP-B 636 155. The polysiloxanes mentioned therein are suitable for manufacturing contact lenses and contain unsaturated hydrocarbon radicals at both chain ends. Such polysiloxanes are unsuitable for the treatment of textile fiber materials in a number of cases because of the reactivity of the carbon-carbon multiple bonds.

It is further known to treat textiles with aqueous dispersions comprising polyorganosiloxanes and polymers containing perfluoroalkyl (R_F) groups. R_F -containing polymers can impart oil-repellent properties to textile fabrics. For instance, US 4 004 059 describes polyorganosiloxanes which, in combination with polymers containing fluorine atoms, are suitable for treating textile fabrics. The polysiloxanes mentioned therein contain relatively long-chain alkyl groups, but no aromatic groups. The disadvantage of these polysiloxanes is that in a number of cases it is difficult or impossible to obtain stable aqueous dispersions comprising these polysiloxanes with or without fluoropolymers. This typically becomes all the more apparent the longer the alkyl chain present as a side chain to the polysiloxane chain.

WO 99/52965 discloses polysiloxanes containing aromatic groups which are attached to silicon atoms via alkylene bridges. They are used for compositions in the cosmetics or perfume sector. As well as the aralkyl groups mentioned, they may further contain alkyl groups having a chain length of up to eight carbon atoms. The use of the described polyorganosiloxanes for treating fiber materials and compositions which, as well as the polysiloxanes, comprise an R_F -containing polymer or a polyurethane are not described in this reference.

US 4 625 010 describes polysiloxanes which, together with fluorine-containing polymers, are suitable for treating textiles. The polysiloxanes contain epoxy units as well as alkyl and aryl groups. The disadvantage of these polysiloxanes resides in the presence of epoxy units, which are in many cases undesirable for textile finishing because of their reactivity. In addition, their

synthesis requires the use of epoxy-containing starting materials, which constitutes a disadvantage on account of the handling of epoxy compounds.

It is an object of the present invention to provide a composition which does not have the abovementioned disadvantages and which in the form of aqueous dispersions is very useful for treating fiber materials, especially textile fabrics.

This object is achieved by a composition comprising the following components:

A) a dispersant or a mixture of dispersants,

B) an unbranched polyorganosiloxane which contains no epoxy groups and no olefinic carbon-carbon double bonds and no carbon-carbon triple bonds, which is terminated, at both ends of the polysiloxane chain, by units of the formula

R_3Si-O-

and which contains, within the polysiloxane chain, units of the formulae (I), (II) and optionally (III)

$-SiRR^1-O-$ (I)

$-SiRR^2-O-$ (II)

$-SiR_2-O-$ (III)

which units of the formulae (I) to (III) may be randomly distributed along the chain,

where each R radical is independently of the other R radicals a branched or unbranched alkyl radical of 1 to 4 carbon atoms,

each R^1 radical is independently of the other R^1 radicals a branched or unbranched alkyl radical of 6 to 24 carbon atoms,

and each R^2 radical is independently of the other R^2 radicals a radical of the formula (IV)

$-R^3-Ph,$ (IV)

where R^3 is a divalent branched or unbranched alkylene radical of 2 to 6 carbon atoms and Ph is an unsubstituted phenyl radical or is a phenyl radical substituted by one or more branched or unbranched alkyl groups of 1 to 4 carbon atoms, and

C) a polymer selected from the group consisting of polymers containing perfluoroalkyl (R_F) groups (component C1) and fluorine-free polyurethanes (component C2).

Compositions according to the invention can optionally be present in the form of a dispersion or solution in an organic solvent and be used for example for the solvent coating of textiles, in which case they additionally comprise customary additives known from the technology of solvent coating. However, a preferred embodiment comprises their presence in the form of

aqueous dispersions and their use as such. For this reason, the statements which follow relate to compositions according to the invention which are in the form of aqueous dispersions.

Dispersions according to the invention have the following advantages:

- a) They can be prepared, by generally customary methods and by using known dispersants, in the form of very stable aqueous dispersions which are very useful for treating textile fabrics, especially wovens and knits.
- b) They confer a pleasantly soft hand and water-repellent properties on textile fiber materials.
- c) They are in the form of stable aqueous dispersions which comprise a component C1), ie one or more polymers containing perfluoroalkyl (R_F) groups, very useful for treating textile fiber materials which may thereby be given a soft hand and also oil- and water-repellent properties.
- d) When they contain one or more fluorine-free polyurethanes (component C2)), they are useful for coating textile fiber materials, in which case the dispersions normally additionally comprise thickeners and are preferably used in the form of highly viscous liquids or pastes.

Preferably, dispersions according to the invention comprise as component C) only one or more components C1), ie one or more polymers which fall within the definition of C1), but no component C2), or they comprise only one or more components C2), but no component C1). In the first case, they are very useful for the oil- and water-repellent finishing of textile fabrics, for example by padding. The textiles additionally acquire a pleasantly soft hand as a result. In the second case, the dispersions are particularly useful for coating textile fabrics and preferably comprise further ingredients such as thickeners, for example.

It has been determined that the polyorganosiloxanes suitable as component B) will lead to the aforementioned advantages to a marked extent when they contain aromatic groups (R^2) in side chains to the polysiloxane chain as well as relatively long-chain alkyl groups (R^1). In the absence of an aromatic group in component B), the preparation of stable aqueous dispersions is frequently very difficult, if not impossible, especially when the number of carbon atoms in the R^1 radical increases. The absence of R^1 radicals does not lead to an ideal soft hand nor frequently to ideal water-repellent properties for finished textiles.

The polyorganosiloxanes used as component B) of dispersions according to the invention are unbranched. This means that the polyorganosiloxane chain has side chains (R^1 and R^2), but no side chains containing silicon atoms.

The polyorganosiloxanes (component B) contain no epoxy groups, no olefinic carbon-carbon double bonds and no carbon-carbon triple bonds. The presence of such reactive groups would compromise usefulness for a number of applications. Nor, for the same reason, do the polyorganosiloxanes preferably contain any Si-H bonds with the exception of low fractions due to their synthesis (which is preferably carried out using siloxanes having Si-H bonds as starting materials). The presence of polyoxyethylene groups in the polyorganosiloxanes is likewise less preferable, since the water-repellent properties of finished textiles can be compromised as a result. However, the polyorganosiloxanes included in compositions according to the invention can still contain minor fractions of Si-OH bonds which are present in the form of by-products from the synthesis.

The polyorganosiloxanes used as component B) of dispersions according to the invention have at each chain end a unit of the formula



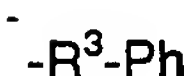
Each R radical is independently of the other R radicals a branched or unbranched alkyl radical of 1 to 4 carbon atoms. Preferably, each R radical is methyl. This definition for R and for the preferred embodiment whereby all R radicals are methyl groups also applies to the hereinbelow described units of the formulae (I), (II) and (III).

The polysiloxane chain of component B) contains internal units of the formula (I), of the formula (II) and optionally additionally of the formula (III). These individual units can be randomly distributed along the polysiloxane chain.

In the units of the formulae (I) and (II), the R^1 and R^2 radicals respectively are present as side chains to the polysiloxane chain.

Each R^1 radical is independently of the other R^1 radicals a branched or unbranched alkyl radical of 6 to 24 carbon atoms. Preferably each R^1 radical is an unbranched alkyl radical of 10 to 18 carbon atoms.

Each R^2 radical is independently of the other R^2 radicals a radical of the formula (IV)



where R^3 is a divalent branched or unbranched alkyl radical of 2 to 6 carbon atoms and Ph is either unsubstituted phenyl or a phenyl substituted on the aromatic ring by one or more branched or branched alkyl groups having 1 to 4 carbon atoms. Preferably, each R^2 radical is



where R^4 is hydrogen or a methyl group and Ph is unsubstituted phenyl.

Preferred dispersions according to the invention are characterized in that in component B), the number of units of the formula (II) is 4 to 30% of the number of units of the formula (I) and the number of units of the formula (III) is 0 to 5 000% and preferably 0 to 1 000% of the number of units of the formula (I).

The numbers of the individual units can be controlled by the amounts of the starting compounds used in the synthesis of the polysiloxanes. A suitable method of synthesis is described hereinbelow.

A further preferred embodiment of dispersions according to the invention is characterized in that component B) contains 20 to 1 000 and preferably 20 to 100 silicon atoms.

The preparation of polysiloxanes useful as component B) can be effected by the following method:

The starting material used is a polysiloxane which has a radical of the formula $\text{R}_3\text{Si}-\text{O}-$ at each chain end and which, in the chain, contains only units of the formula



Such polysiloxanes (hydrosiloxanes) are commercially available; an example is the "Finish WS 61 M" product (from Wacker, Germany) or the "HMS 301" product (from ABCR GmbH, Germany). To prepare polyorganosiloxanes according to the invention, the hydrosiloxane mentioned is reacted not only with a monoolefin of 6 to 24 carbon atoms but also with an aromatic compound. The $\text{C}=\text{C}$ double bond of the C_6 - C_{24} -monoolefin can be terminal or internal to the hydrocarbon chain; preferably it is terminal. The aromatic compound contains a benzene nucleus which is substituted by at least one substituent. This substituent is a linear or branched hydrocarbon radical of 2 to 6 carbon atoms which contains one $\text{C}=\text{C}$ double bond. In addition, the aromatic compound can be substituted on the benzene nucleus by one or more linear or

branched alkyl groups of 1 to 4 carbon atoms.

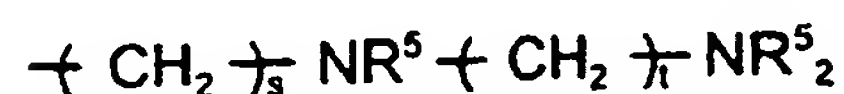
Of particular use for preparing polysiloxanes by the abovementioned processes are monoolefins of 10 to 18 carbon atoms, especially those having a terminal olefinic double bond. An example is 1-dodecene. As to aromatic compounds, styrene and α -methylstyrene are particularly suitable.

Suitable choice of the type and amount of the starting substances mentioned and of the conditions for the synthesis makes it possible to influence the structure of the resulting polyorganosiloxanes in a specific manner, for example with regard to the number of units of the formulae (I), (II) and (III) and with regard to the total number of silicon atoms.

In the reaction mentioned, the hydrosiloxane can be reacted with the monoolefin and the aromatic compound simultaneously. However, it is also possible for the hydrosiloxane to be reacted first with one of these compounds and then with the other. In the reaction, the Si-H group adds to the respective olefinic C=C double bond to form the R¹ and R² radicals in the polysiloxanes according to the invention. Preferably, the reaction is carried out with such amounts of starting materials and under such conditions that the resulting product mixture contains Si-H bonds and olefinic double bonds only to an insignificant extent, if at all. The reaction can be carried out under conditions generally known from hydrosiloxane chemistry.

Polysiloxanes useful as component B) are likewise commercially available. One example is the TEGOPREN 6870 product (from Goldschmidt, Germany).

Component B) of dispersions according to the invention, as well as units of the formulae (I), (II) and optionally (III), may additionally contain amino-containing radicals, especially radicals of the formula



which are each attached to one silicon atom and in which s is from 2 to 6, preferably 3, t is from 2 to 6, preferably 2, and each R⁵ radical is independently of the other R⁵ radicals hydrogen or an alkyl group of 1 to 4 carbon atoms. The introduction of such radicals into component B) is accomplished by reacting, in the course of the above-described synthesis, the hydrosiloxane not only with an olefin and an aromatic compound, but additionally with an unsaturated aliphatic amine, for example allylamine or N-(2-aminoethyl)allylamine. The reaction with the allylamine can take place simultaneously with the reaction with olefin and aromatic compound or beforehand or afterwards.

Preferably, component A) (dispersant or dispersant mixture) of dispersions according to the invention is exclusively selected from nonionic surface-active compounds. Suitable dispersants will be known to one skilled in the art of silicone emulsions and are commercially available. Especially ethoxylated fatty alcohols or ethoxylated fatty acids may be mentioned in this context, for example those having 8 to 18 carbon atoms in the alkyl radical which can be linear or branched, or having 6 to 20 polyoxyethylene units. These ethoxylates can be terminated at one end of the chain by an OH group or an OR group, where R is an alkyl of 1 to 4 carbon atoms, especially CH₃.

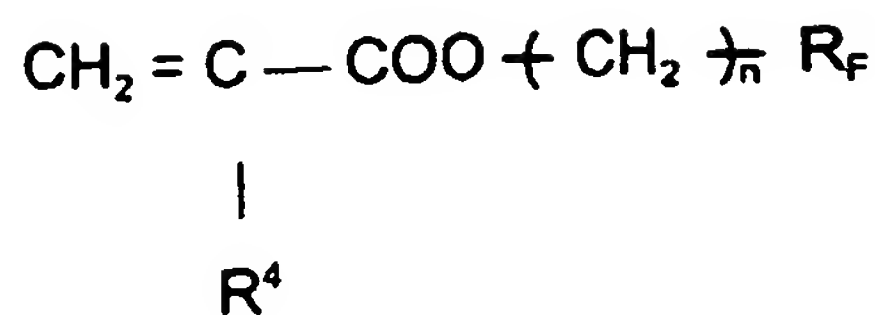
If desired, dispersions according to the invention can be prepared by mixing an aqueous dispersion of a component B) with an aqueous dispersion of a component C1) or a component C2), provided at least one of these dispersions already contains component A). Since the commercially available dispersions of a component C1) or of a component C2) can contain ionic, for example cationic, dispersants, it will be appreciated that their use means that the resulting dispersions according to the invention also contain ionic dispersants.

Dispersions according to the invention, as well as the above-described components A) and B), additionally contain a component C). Component C) can be a polymer or a mixture of polymers which contains perfluoroalkyl (R_F) groups; such polymers will hereinafter be referred to as component C1). They can also be a fluorine-free polyurethane or a mixture of such polyurethanes which hereinafter is referred to as component C2). Preferably, dispersions according to the invention contain as component C) either only polymers which fall within the definition of C1) and are preferably used for padding textile fabrics; or else they contain as component C) only polyurethanes as per the definition of C2) and are preferably used for coating textile fabrics. In either case the textile fabrics preferably take the form of wovens or knits.

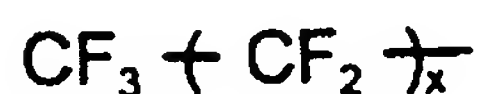
Preferably, dispersions according to the invention comprise 0.5 to 10% by weight of component A), 0.5 to 30% by weight of component B), 3 to 30% by weight of component C) and 30 to 96% by weight of water.

Component C1) is preferably a polyester having R_F groups, a polyurethane having R_F groups, a polyacrylate having R_F groups or a mixture thereof. Such polymers are commercially available, an example being the ZONYL products (from Du Pont).

Useful polyacrylates having R_F groups include in particular homopolymers or copolymers obtainable from monomers of the formula



where R⁴ is H or CH₃, n is from 2 to 6 and R_F is a perfluoroalkyl radical of the formula



where x is from 5 to 19. Here it is normal to use a mixture of acrylates of this formula whose individual compounds differ in the chain length of R_F. Copolymers based on the abovementioned monomer which are highly suitable for use as component C1) are obtainable by copolymerizing this monomer with one or more of the following monomers: vinyl chloride, vinylidene chloride, butyl acrylate, butyl methacrylate, stearyl (meth)acrylate.

Suitable R_F-containing polyacrylates are also described in US 4 742 140.

Polyurethanes having R_F groups and being highly suitable for use as component C1) are obtainable by reacting diols which contain one or more R_F groups with diisocyanates. Fluorine-free diols may additionally be used in this reaction as chain extenders, examples of the fluorine-free diols which can be used being N-methyldiethanolamine or polyglycols. A particularly suitable R_F-containing diol is a product of the formula



where R_F is as defined above and n is from 2 to 6. It is normal here to use a mixture of diols of this formula whose individual compounds differ in the chain length of R_F . These diols and their preparation and also the preparation of R_F polyurethanes are described in the literature, for example in EP-A 459 125 and EP-A 348 350. Further suitable R_F diols and their reaction with diisocyanates to form R_F -containing polyurethanes are described in EP-A 1 088 929 (component B) of claim 1) and in US 4 054 592.

R_F-containing polyesters which are highly suitable for use as component C1) are known and are described for example in EP-A 1 088 929 (component A) of claim 1). Particularly suitable polyesters are obtainable from the abovementioned preferred R_F diols and aliphatic dicarboxylic acids such as adipic acid for example.

As component C1) it is also possible to use R_F-containing polyurethanes which are copolymers having urethane and having siloxane units. Such polymers are described in EP-A 325 918 and

EP-A 467 083.

Component C2) of dispersions according to the invention is a fluorine-free polyurethane. Polyurethanes useful for this purpose are preparable from diols and diisocyanates by methods which are common knowledge from polyurethane chemistry. Preference is given to using polyurethanes which no longer contain any free isocyanate groups, which is controllable via the preparative conditions, for example through the use of a certain excess of diol OH groups over diisocyanate isocyanate groups.

Polyurethanes which are very useful as component C2) are obtainable from the following diols by reaction with diisocyanates: ethylene glycol and its homologues of 3 to 50 carbon atoms such as for example low molecular weight diols or polyethylene glycols having a molecular weight of 400 to 800. The carbon chains of the diols can be linear or branched. It is also possible to use mixtures of such diols in the preparation.

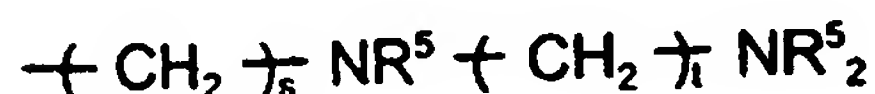
The reaction with diols to form polyurethanes useful as component C2) can be carried out with aliphatic, cycloaliphatic or aromatic diisocyanates. Examples which are very useful are hexamethylene 1,6-diisocyanate, trimethylhexylmethylen 1,6-diisocyanate (for example as mixture of isomers), 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate or a mixture thereof. Polyurethanes of the kind mentioned are commercially available.

Polyurethanes which are particularly useful as component C2) are polyester urethanes. These contain polyester units in the polymer chain as well as urethane units. They are preparable by known methods by reacting polyesters which have free OH groups at the chain ends with diisocyanates. Diols are advantageously additionally used in this reaction as chain extenders. Useful diols and diisocyanates for this reaction include the compounds already described above. The polyesters having free OH end groups that are used for the synthesis can be aliphatic or aromatic compounds. Highly suitable polyesters are obtainable by reacting terephthalic acid, phthalic acid or an aliphatic dicarboxylic acid of 2 to 6 carbon atoms with an excess of diol. The diol used for this purpose can again be of the type described above. The preparation of polyester urethanes which are very useful as component C2) is described for example in EP-A 1 055 692, EP-A 1 010 712 and EP-A 295 422.

Useful polyester urethanes are commercially available in the form of aqueous dispersions. These dispersions which, as well as polyester polyurethanes (component C2), additionally contain dispersants are generally ready to use for the preparation of dispersions according to the invention without prior isolation of the polyester polyurethane. Examples of such commercial products are IMPRANIL DLN Dispersion W 50 (from Bayer AG) and BAYDERM Grund 10 UD (from Bayer AG).

If desired, dispersions according to the invention can contain further components of the kind

customarily used for treating textile fabrics. Examples thereof are flame retardants or cellulose crosslinkers. Also, further polyorganosiloxanes can be present besides component B). These should be substantially free of carbon-carbon multiple bonds, of epoxy groups, of polyalkylene oxide groups and of Si-H bonds. Polyorganosiloxanes useful for this purpose include polydimethylsiloxanes having $(\text{CH}_3)_3\text{Si-O-}$ end groups or polydimethylsiloxanes where one or more methyl groups in the polymer chain (but not two methyl groups on the same silicon atom) are replaced by amino-containing radicals. These radicals are preferably the above-described radicals of the formula



Such amino-functional polysiloxanes are known from the prior art and can be prepared from hydrosiloxanes and unsaturated amines, for example allylamines. Useful products of this kind are obtainable from Wacker, Germany, and from Dow Corning. Suitable commercially available amino-functional polysiloxanes are either already in the form of aqueous dispersions or can be converted into aqueous dispersions by generally known methods. These aqueous dispersions can be added to dispersions according to the invention. Suitable amino-functional polysiloxanes and aqueous dispersions thereof are described in US 4 247 592, EP-A 138 192 and WO 88/08436.

It is frequently of advantage for dispersions according to the invention which contain a component C1) to additionally contain an extender or a mixture of extenders. Extenders enhance the oil/water-repellent properties of textiles finished with fluoropolymers and so make it possible for an effective performance level to be achieved even at comparatively low use levels of (costly) fluoropolymers.

Extenders and their use in the treatment of textiles with fluoropolymers are known from the prior art. Useful extenders are in particular compounds which contain reversibly blocked isocyanate groups. These reversibly blocked isocyanates are converted back to free isocyanate groups at elevated temperature. Useful blocking agents include in particular ketone oximes, for example butanone oxime.

Useful extenders are in particular aliphatic, cycloaliphatic and aromatic compounds having two or more blocked isocyanate groups, for example hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, diphenylmethane 4,4'-diisocyanate, each after blocking of the NCO groups.

Useful extenders are described in EP-A 872 503 (claim 1), EP-A 537 578 (claim 1) and WO 86/02115.

Useful extenders further include commercially available products after the free isocyanate groups of these products have been blocked, for example by reaction with a ketone oxime. Examples of such commercial products are BAYGARD EDW and DESMODUR L 75 (NCO-containing polyurethanes from Bayer, Germany) and also "isophorone diisocyanate" (= 1-methyl, 1-isocyanatomethyl-, 3-isocyanato-5,5-dimethylcyclohexane).

When dispersions according to the invention which contain a component C1) are to additionally contain an extender, the extender is preferably added in such amounts that the weight ratio of component C1) to extender is in the range from 1:0.1 to 1:1.5, especially in the range from 1:0.2 to 1:0.8.

Dispersions according to the invention can be prepared by generally known methods. One way is to initially charge a mixture of water and component A) (dispersant), to add the other components and then to mechanically homogenize. Normally, stable dispersions are obtainable at room temperature, but in certain circumstances a somewhat elevated temperature may be required.

Dispersions according to the invention which contain the components A), B) and C1) as well as water are especially useful for pad-mangle application to textile fabrics such as wovens or knits composed of cotton, synthetics such as polyester or nylon, or blends thereof. The textile fabrics thus finished are useful for manufacturing garments or home textiles. Application via pad-mangle and further processing of finished textiles can be effected in accordance with customary processes.

Dispersions according to the invention which contain the components A), B) and C2) as well as water are useful for coating textile fabrics such as for example wovens composed of cotton, linen, synthetics such as polyester or nylon or fiber blends for final articles such as fashionable coated clothing. To this end, the dispersions are normally admixed with thickeners, as is customary for coating processes. In addition, foam-inhibiting products can be used in the preparation of the dispersions.

A suitable coating recipe is obtainable for example by admixing 1 000 parts by weight of an aqueous dispersion containing the components A), B), C2) and water with 5 parts by weight of a defoamer, followed by a thickener in such an amount as to provide a highly viscous liquid or a pasty consistency of the kind customarily used for coating operations. An example of a useful defoamer is the DICRYLAN-Entschäumer D product from Ciba Spezialitätenchemie Pferssee GmbH, Germany, a composition based on a hydrocarbon mixture. Silicone defoamers can also be used.

Useful thickeners include polyacrylate-based products such as DICRYLAN-Verdicker TFC or DICRYLAN-Verdicker R (Ciba Spezialitätenchemie Pferssee GmbH, Germany). In the case of the use of DICRYLAN-Verdicker R, the pH should be adjusted to a weakly basic value, for example by means of ammonia. Coating and further processing can be carried out in accordance with the customary processes.

The examples hereinbelow illustrate the invention.

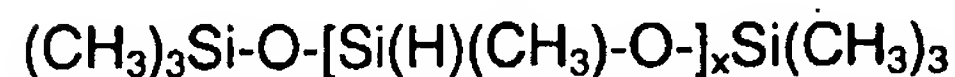
Example 1

Preparation of a component B) (polyorganosiloxane)

A three-neck flask was charged with 60 g of hydrosiloxane (see below for structure), 100 g of 1-dodecene and 8 g of α -methylstyrene. 1 ml of a mixture of 37 g of 1-dodecene and 0.5 g of a catalyst was added with stirring while N_2 was passed in. In the process, the temperature of the mixture rose from room temperature to about 120°C. The remainder of the mixture of 1-dodecene and catalyst was then added at 80°C. The time over which the total amount of this mixture was added was about 70 minutes. The product mixture was subsequently stirred at 80°C for a further 260 minutes or so.

This afforded a slightly yellow liquid having a viscosity of about 1 100 mPas (at 25°C). The polyorganosiloxane present in the liquid had a unit of the formula $(CH_3)_3Si-O-$ at each chain end and contained units of the formula $-Si(CH_3)(-C_{12}H_{25})-O-$ and units of the formula $-Si(CH_3)(-CH_2-CH(CH_3)-C_6H_5)-O-$ within the chain.

The abovementioned catalyst was a solution of a platinum(0) complex of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane in isopropanol. This solution contained about 1% of Pt. The hydrosiloxane (from Wacker, Germany) had the following structure:



where x is about 40.

Example 2

Preparation of an aqueous dispersion of a component B)

175 g of the product obtained according to example 1 were introduced into a mixture of 20 g of water and 15 g of an ethoxylated C_{10}/C_{14} alcohol (about 6 polyoxyethylene units). The mixture

was homogenized by vigorous stirring at room temperature, after which 290 g of water and 0.5 g of a bactericide were added. This afforded a stable opalescent aqueous dispersion (= "dispersion 1").

Example 3

Preparation of an aqueous dispersion of a component B) and of an amino-functional polysiloxane

18 g of an amino-functional polysiloxane (Q2-8630, Dow Corning) and 157 g of the reaction product obtained as per example 1 were introduced into a solution of 15 g of ethoxylated C₁₀/C₁₄ alcohol (see example 2) in 20 g of water and the mixture obtained was homogenized by vigorous stirring at room temperature. 2.5 g of a 60% solution of acetic acid in water were then added, followed by 290 g of water and 0.5 g of a bactericide. Renewed homogenization provided a stable opalescent aqueous dispersion (= "dispersion 2").

Example 4 (noninventive, comparative example)

This example constitutes an attempt to obtain a stable aqueous dispersion of a polysiloxane which contained comparatively long alkyl radicals but no aromatic groups in side chains. To this end, 45 g of hydrosiloxane (see example 1) were added over 70 minutes to a mixture containing 111 g of 1-dodecene and 0.6 g of catalyst based on a platinum complex of divinylsiloxane. The mixture was subsequently stirred at 80°C for 2.5 hours under N₂. This provided a yellowish liquid having a viscosity of about 700 mPa.s (at 25°C). 126 g of the product mixture thus obtained were stirred into a solution of 11 g of ethoxylated alcohol (see example 2) in 15 g of water. 208 g of water and 0.4 g of bactericide were then added. It proved impossible to obtain a stable dispersion even after prolonged intensive stirring.

Example 5

Preparation of an aqueous dispersion according to the invention

0.5 g of an ethoxylated alcohol (alkyl chain on average 13 carbon atoms and 20 polyoxyethylene units) was dissolved in 4 g of water with stirring and the mixture was heated to 60°C.

1.5 g of the ethoxylated alcohol described in example 2 were then added and the mixture was stirred at 60°C until a clear solution had formed. This solution was cooled to 30°C, at which

point 48 g of an aqueous polyurethane dispersion and 48 g of dispersion 1 obtained as per example 2 were added with stirring. This provided a milky dispersion which was very stable even after 30 days of storage at 40°C or at room temperature and which, after addition of a thickener, was very useful for coating textile fiber materials.

The aqueous polyurethane dispersion used was the DICRYLAN PSC product (from Ciba Spezialitätenchemie Pforzheim GmbH, Germany) and contained 70% of water and 30% of a polyester urethane based on an aliphatic diisocyanate and a polyester based on a mixture of an aromatic and an aliphatic dicarboxylic acid and an aliphatic diol, the polyester still containing free OH groups.

Useful thickeners for preparing a coating recipe include the acrylate-based polymers mentioned above in the description part.

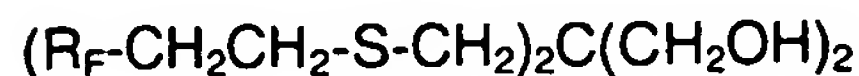
Example 6

Preparation of a dispersion according to the invention

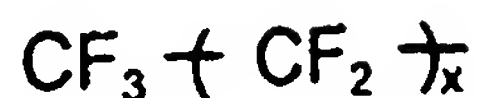
The hereinbelow described products a) to e) were mixed with each other at room temperature and the mixture was homogenized by stirring.

- a) 107 g of an aqueous beige-colored dispersion comprising 16% by weight of an acrylic copolymer which contained R_F groups, 3% by weight of an aliphatic diol of 6 carbon atoms, 1.5% by weight of polyethylene glycol monostearate and 80% by weight of water.
- b) 107 g of an aqueous dispersion comprising 14% by weight of a polyurethane which contained R_F groups, 7% by weight of a butanone oxime blocked polyisocyanate, 1.5% by weight of an ethoxylated isotridecyl alcohol containing 10 EO units on average, 0.7% by weight of polyoxyethylenestearyltrimethylammonium chloride, 3% by weight of 1,2-propanediol, 0.1% by weight of HCl, remainder water.

The R_F -containing polyurethane used for this purpose was a product obtained by reaction of

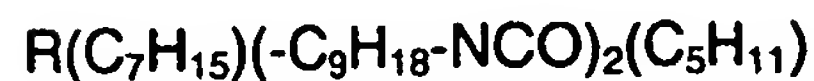


with trimethylhexamethylene diisocyanate (mixture of isomers). The R_F radicals conformed to the formula



where x is on average in the range from 7 to 11.

The butanone oxime blocked polyisocyanate was prepared on the basis of



where R is the tetravalent radical formed from cyclohexane by removal of 4 hydrogen atoms.

- c) 12 g of dispersion 1 as per example 2
- d) 12 g of isobutyl ether of a reaction product of tallow fatty amine, urea and formaldehyde
- e) 12 g of water

This provided a stable aqueous dispersion (= "dispersion 3")

Example 7

Example 6 was repeated, except that product c) was not dispersion 1 but 12 g of dispersion 2 as per example 3. This provided a stable dispersion (= "dispersion 4")

Example 8

The hereinbelow described products f) to j) were mixed at room temperature and the mixture was homogenized by stirring.

- f) 80 g of product a) of example 6
- g) 80 g of an aqueous dispersion comprising 15% by weight of an R_F-containing acrylic polymer, 2% by weight of polyoxyethylene glycol monostearate, 8% by weight of acetone, 5% by weight of an aliphatic diol of 6 carbon atoms and 70% by weight of water
- h) 15 g of dispersion 1 as per example 2

- i) 15 g of product d) of example 6
- j) 10 g of water

This again provided a stable aqueous dispersion (= "dispersion 5")

Example 9

Example 8 was repeated, except that product h) was not dispersion 1 but 15 g of dispersion 2 as per example 3. The result was a stable dispersion (= "dispersion 6").

Example 10

Finishing tests on wovens composed of 100% cotton and on polyester-cotton blend fabrics

Dispersions 3 and 4 as per examples 6 and 7 were padded onto wovens composed of 100% cotton and onto wovens composed of (40:60) cotton-polyester. The liquor concentrations used were 10 g/l, 20 g/l and 40 g/l. After liquor application, the fabrics were squeezed off to about 80% wet pick-up, dried (10 min/110°C) and cured (5 min/150°C).

The comparison in each case was a woven fabric to which there was applied a dispersion which corresponded to dispersion 3 of example 6, except that product c) (= dispersion 1) had not been added. Instead, this comparative dispersion included 12 g of an aqueous dispersion containing 35% of a polyorganosiloxane and 3% by weight of a dispersant (C₁₀/C₁₄ alcohol ethoxylated, about 6 EO units). The polyorganosiloxane used contained Si-H bonds and epoxy groups and also alkyl groups and aromatic groups in side chains.

Tests on the fabrics showed in the case of 100% cotton that the dispersions according to the invention led to substantially the same values with regard to oil repellency than the comparative fabric, but to distinctly better values with regard to water repellency (Bundesmann test). In the case of blend fabric, the corresponding results were somewhat better.

WHAT IS CLAIMED IS:

1. A composition comprising the following components:

A) a dispersant or a mixture of dispersants,

B) an unbranched polyorganosiloxane which contains no epoxy groups and no olefinic carbon-carbon double bonds and no carbon-carbon triple bonds, which is terminated, at both ends of the polysiloxane chain, by units of the formula



and which contains, within the polysiloxane chain, units of the formulae (I), (II) and optionally (III)



which units of the formulae (I) to (III) may be randomly distributed along the chain,

where each R radical is independently of the other R radicals a branched or unbranched alkyl radical of 1 to 4 carbon atoms,

each R^1 radical is independently of the other R^1 radicals a branched or unbranched alkyl radical of 6 to 24 carbon atoms,

and each R^2 radical is independently of the other R^2 radicals a radical of the formula (IV)



where R^3 is a divalent branched or unbranched alkylene radical of 2 to 6 carbon atoms and Ph is an unsubstituted phenyl radical or is a phenyl radical substituted by one or more branched or unbranched alkyl groups of 1 to 4 carbon atoms, and

C) a polymer selected from the group consisting of polymers containing perfluoroalkyl (R_F) groups (component C1) and fluorine-free polyurethanes (component C2).

2. A composition according to claim 1, characterized in that each R in component B) is methyl.

3. A composition according to claim 1 or 2, characterized in that each R^1 radical in component B) is independently of other R^1 radicals an unbranched alkyl radical of 10 to 18 carbon atoms.

4. A composition according to one or more of claims 1 to 3, characterized in that each R^2 radical in component B) is



where R^4 is hydrogen or a methyl group and Ph is unsubstituted phenyl.

5. A composition according to one or more of claims 1 to 4, characterized in that, in component B), the number of units of the formula (II) is 4 to 30% of the number of units of the formula (I) and the number of units of the formula (III) is 0 to 5 000% and preferably 0 to 1 000% of the number of units of the formula (I).
6. A composition according to one or more of claims 1 to 5, characterized in that component B) contains 20 to 1 000 and preferably 20 to 100 silicon atoms.
7. A composition according to one or more of claims 1 to 6, characterized in that it comprises 0.5 to 10% by weight of component A), 0.5 to 30% by weight of component B), 3 to 30% by weight of component C) and 30 to 96% by weight of water.
8. A composition according to one or more of claims 1 to 7, characterized in that component A) consists exclusively of nonionic compounds.
9. A composition according to one or more of claims 1 to 8, characterized in that component C) comprises either only one or more of components C1) or only one or more components C2).
10. A composition according to one or more of claims 1 to 9, characterized in that component C1) is a polyester, a polyurethane or a polyacrylate which contains R_F groups.
11. A composition according to one or more of claims 1 to 9, characterized in that C2) is a polyester urethane.
12. A composition according to one or more of claims 1 to 11, characterized in that it is an aqueous dispersion.
13. The use of a dispersion according to claim 12 for treating fiber materials.
14. The use according to claim 13, characterized in that the fiber materials are textile fabrics in the form of wovens or knits.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/05628

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L83/04 D06M15/643 //(C08L83/04,C08L57:06),(C08L83/04,
C08L75:04)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 121 078 A (BAYER AG) 10 October 1984 (1984-10-10) claims 1-5 ---	1-14
A	WO 99 52965 A (BRANLARD PAUL ;MIGNANI GERARD (FR); OLIER PHILIPPE (FR); RHONE POU) 21 October 1999 (1999-10-21) cited in the application claims 1-13 ---	1-12
A	US 4 004 059 A (DEINER HANS ET AL) 18 January 1977 (1977-01-18) cited in the application column 5, line 58 -column 7, line 16; claims 1-9 -----	1-14

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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26 August 2002

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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